

## Module 2

# SOIL-WATER-CONTAMINANT INTERACTION

Knowledge of soil-water interaction and soil-water-contaminant interaction is very important for solving several problems encountered in geoenvironmental engineering projects. The following section introduces soil mineralogy and various mechanisms governing soil-water-contaminant interaction.

### **2.1 Soil mineralogy characterization and its significance in determining soil behaviour**

Soil is formed by the process of weathering of rocks which has great variability in its chemical composition. Therefore, it is expected that soil properties are also bound to the chemical variability of its constituents. Soil contains almost all type of elements, the most important being oxygen, silicon, hydrogen, aluminium, calcium, sodium, potassium, magnesium and carbon (99 percent of solid mass of soil). Atoms of these elements form different crystalline arrangement to yield the common minerals with which soil is made up of. Soil in general is made up of minerals (solids), liquid (water containing dissolved solids and gases), organic compounds (soluble and immiscible), and gases (air or other gases). This section deals with the formation of soil minerals, its characterization and its significance in determining soil behaviour.

#### **2.1.1 Formation of soil minerals**

Based on their origin, minerals are classified into two classes: primary and secondary minerals (Berkowitz et al. 2008). Primary minerals are those which are not altered chemically since the time of formation and deposition. This group includes quartz ( $\text{SiO}_2$ ), feldspar ( $(\text{Na,K})\text{AlSi}_3\text{O}_8$  aluminosilicates containing varying amounts of sodium, potassium), micas (muscovite, chlorite), amphibole (hornblende: magnesium iron silicates) etc. Secondary minerals are formed by

the decomposition and chemical alteration of primary minerals. Some of these minerals include kaolinite, smectite, vermiculite, gibbsite, calcite, gypsum etc. These secondary minerals are mostly layered alumino-silicates, which are made up of silicon/oxygen tetrahedral sheets and aluminium/oxygen octahedral sheets. Primary minerals are non-clay minerals with low surface area (silica minerals) and with low reactivity (Berkowitz et al. 2008). These minerals mainly affect the physical transport of liquid and vapours (Berkowitz et al. 2008). Secondary minerals are clay minerals with high surface area and high reactivity that affect the chemical transport of liquid and vapours (Low 1961).

Silica minerals are classified as tectosilicates formed by  $\text{SiO}_4$  units in frame like structure. Quartz, which is one of the most abundant minerals comprises up to 95percent of sand fraction and consists of silica minerals. The amount of silica mineral is dependent upon parent material and degree of weathering. Quartz is rounded or angular due to physical attrition. The dense packing of crystal structure and high activation energy required to alter Si-O-Si bond induce very high stability of quartz. Therefore, the uncertainty associated with these materials is minimal. In the subsurface, quartz is present in chemically precipitated forms associated with carbonates or carbonate-cemented sandstones.

Clay minerals, which can be visualized as natural nanomaterials are of great importance to geotechnical and geoenvironmental engineers due to the more complex behaviour it exhibits. Therefore, this chapter emphasise more on understanding clay mineral formation and its important characteristics. Basic units of clay minerals include silica tetrahedral unit and octahedral unit depicted in Fig. 2.1.

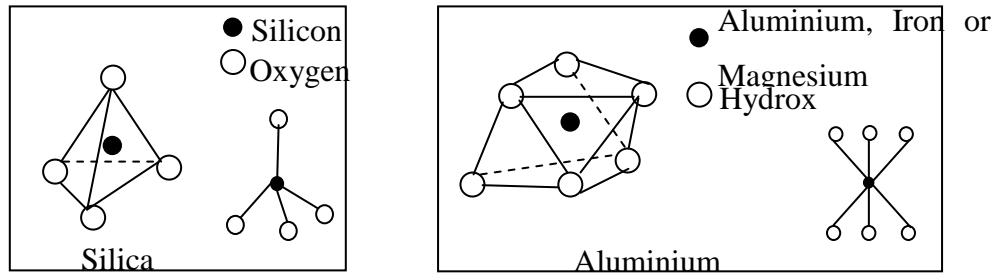
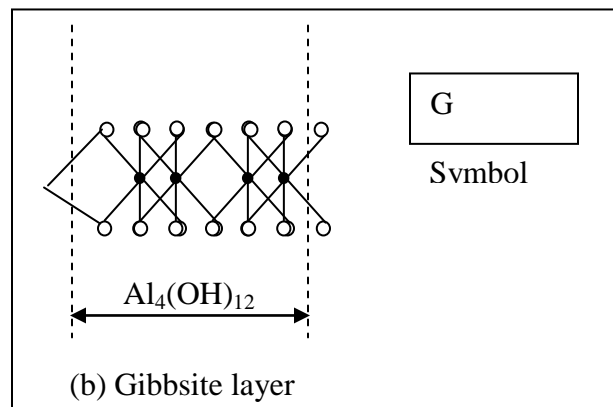
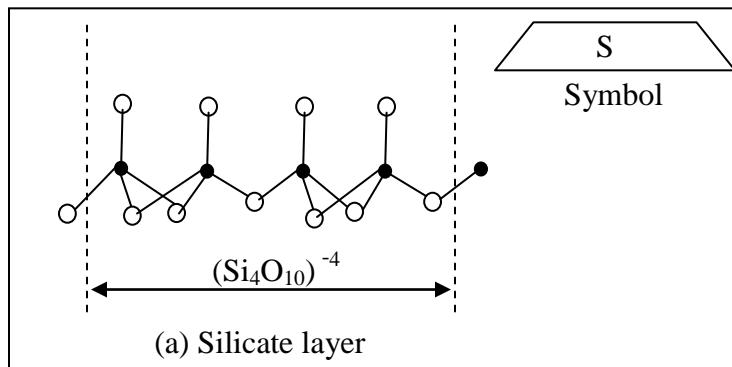


Fig. 2.1 Basic units of clay minerals (modified from Mitchell and Soga 2005)

It can be noted from the figure that metallic positive ion is surrounded by non-metallic outer ions. Fig. 2.2 shows the formation of basic layer from basic units indicated in Fig. 2.1. There are 3 layers formed such as (a) silicate layer, (b) gibbsite layer and (c) brucite layer.



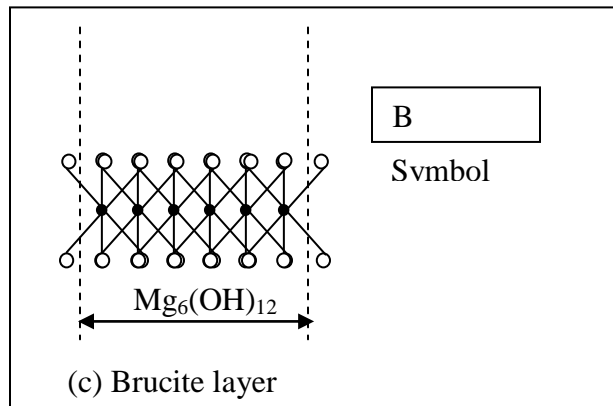


Fig. 2.2 Basic layer of mineral formation (modified from Mitchell and Soga 2005)

Gibbsite layer is otherwise termed as dioctahedral structure in which two-third of central portion is occupied by  $Al^{+3}$ . Similarly, brucite layer is termed as trioctahedral structure in which entire central portion is occupied by  $Mg^{+2}$ . These basic layers stack together to form basic clay mineral structure. Accordingly, there is two and three layer configuration as indicated in Fig. 2.3. More than hundreds these fundamental layers join together to form a single clay mineral.

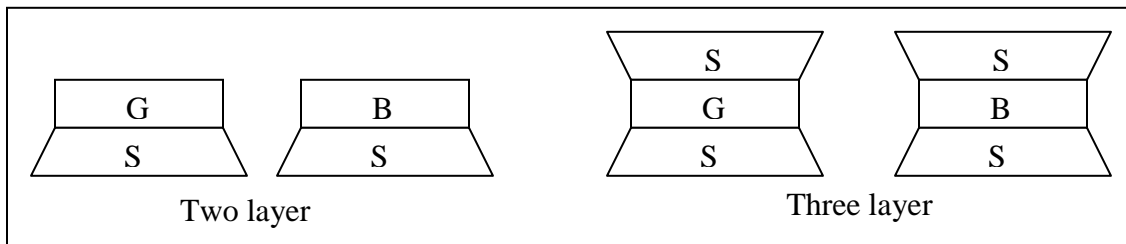
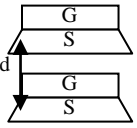
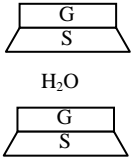
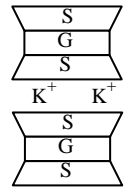
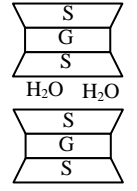
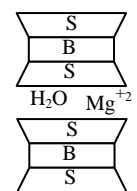


Fig. 2.3 Fundamental layers of clay minerals (modified from Mitchell and Soga 2005)

### Description on common clay minerals

Some of the important and common clay minerals are described below in Table 2.1.

**Table 2.1 Summary of important clay minerals**

Mineral	Origin	Symbol	Bond	Shape	Remark
Kaolinite	Orthoclase Feldspar (Granitic rocks)		Strong hydrogen bond	Flaky and platy	Approximately 100 layers in a regular structure $d = 7.2A^0$
Halloysite (Kaolinite group)	Feldspar Tropical soil		Less strong bond	Tubular or rod like structure	At 60°C it loses water and alters soil properties
Illite	Degradation of mica under marine condition Feldspar		K <sup>+</sup> provides bond between adjacent layers	Thin and small flaky material	Bond is weaker than kaolinite $d = 10A^0$ High stability
Montmorillonite (Smectite group)	Weathering of plagioclase		H <sub>2</sub> O molecules push apart mineral structure causing swelling  Presence of cations	Very small platy or flaky particle	Exhibits high shrinkage and swelling Weak bond $d > 10A^0$
Vermiculite	Weathering of biotite and chlorite		Presence of H <sub>2</sub> O and Mg <sup>+2</sup> predominantly Mg <sup>+2</sup>	Platy or flaky particle	Shrinkage and swelling less than montmorillonite

Kaolinite formation is favoured when there is abundance of alumina and silica is scarce. The favourable condition for kaolinite formation is low electrolyte content, low pH and removal of ions that flocculate silica (such as Mg, Ca and Fe by leaching). Therefore, there is higher probability of kaolinite formation in those regions with heavy rainfall that facilitate leaching of above cations. Similarly halloysite is formed by the leaching of feldspar by  $\text{H}_2\text{SO}_4$  produced by the oxidation of pyrite. Halloysite formations are favoured in high-rain volcanic areas. Smectite group of mineral formation are favoured by high silica availability, high pH, high electrolyte content, presence of more  $\text{Mg}^{+2}$  and  $\text{Ca}^{+2}$  than  $\text{Na}^+$  and  $\text{K}^+$ . The formation is supported by less rainfall and leaching and where evaporation is high (such as in arid regions). For illite formation, potassium is essential in addition to the favourable conditions of smectite.

### ***2.1.2 Important properties of clay minerals***

Some of the important properties that influence the behaviour of clay minerals are presented below:

#### **Specific surface area**

Specific surface area (SSA) is defined as the surface area of soil particles per unit mass (or volume) of dry soil. Its unit is in  $\text{m}^2/\text{g}$  or  $\text{m}^2/\text{m}^3$ . Clay minerals are characterized by high specific surface area (SSA) as listed in Table 2.2. High specific surface area is associated with high soil-water-contaminant interaction, which indicates high reactivity. The reactivity increases in the order Kaolinite < Illite < Montmorillonite. For the purpose of comparison, SSA of silt and sand has also been added in the table. There is a broad range of SSA values of soils, the maximum being for montmorillonite and minimum for sand. As particle size increases SSA decreases.

**Table 2.2 Typical values of SSA for soils (modified from Mitchell and Soga 2005)**

<b>Soil</b>	<b>SSA (m<sup>2</sup>/g)</b>
Kaolinite	10-30
Illite	50-100
Montmorillonite	200-800
Vermiculite	20-400
Silt	0.04-1
Sand	0.001-0.04

For smectite type minerals such as montmorillonite, the primary external surface area amounts to 50 to 120 m<sup>2</sup>/g. SSA inclusive of both primary and secondary surface area, (interlayer surface area exposed due to expanding lattice), and termed as total surface area would be close to 800 m<sup>2</sup>/g. For kaolinite type minerals there is possibility of external surface area where in the interlayer surface area does not contribute much. There are different methods available for determination of external or total specific surface area of soils (Cerato and Lutenegeger 2002, Arnepalli et al. 2008).

## **Plasticity and cohesion**

Clay attracts dipolar water towards its surface by adsorption. This induces plasticity in clay. Therefore, plasticity increases with SSA. Water in clays exhibits negative pressure due to which two particles are held close to each other. Due to this, apparent cohesion is developed in clays.

## **Surface charge and adsorption**

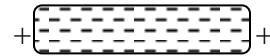
Clay surface is charged due to following reasons:  
 Isomorphous substitution (Mitchell and Soga 2005): During the formation of mineral, the normally found cation is replaced by another due to its abundant availability. For example, when Al<sup>+3</sup> replace Si<sup>+4</sup> there is a shortage of one positive charge, which appears as negative charge on clay surface. Such substitution is therefore the major reason for net negative charge on clay particle surface.

$O^{2-}$  and  $OH^-$  functional groups at edges and basal surface also induce negative charge.

Dissociation of hydroxyl ions or broken bonds at the edges is also responsible for unsatisfied negative or positive charge. Positive charge can occur on the edges of kaolinite plates due to acceptance of  $H^+$  in the acid pH range (Berkowitz et al. 2008). It can be negatively charged under high pH environment.

Absence of cations from the crystal lattice also contributes to charge formation.

In general, clay particle surface are negatively charged and its edges are positively charged.



Typical charged clay

Due to the surface charge, it would adsorb or attract cations (+ve charged) and dipolar molecules like water towards it. As a result, a layer of adsorbed water exists adjacent to clay surface, the details of which are presented in section 2.2.1.

## Exchangeable cations and cation exchange capacity

Due to negative charge, clay surface attracts cations towards it to make the charge neutral. These cations can be replaced by easily available ions present in the pore solution, and are termed as exchangeable ions. The total quantity of exchangeable cations is termed as cation exchange capacity, expressed in milliequivalents per 100 g of dry clay. Cation exchange capacity (CEC) is defined as the unbalanced negative charge existing on the clay surface. Kaolinite exhibits very low cation exchange capacity (CEC) as compared to montmorillonite. Determination of CEC is done after removing all excess soluble salts from the soil. The adsorbed cations are then replaced by a known cation species and the quantity of known cation required to saturate the exchange sites is determined analytically.

## Flocculation and dispersion

When two clay particles come closer to each other it experiences (a) interparticle attraction due to weak van-der-Waal's force (b) repulsion due to  $-ve$



charge. When particles are sufficiently close, attraction becomes dominant active force and hence there is an edge to face configuration for clay particles as shown in Fig. 2.4(a). Such a configuration is termed as flocculant structure. When the separation between clay particles increase, repulsion becomes predominant and hence the clay particles follows face to face configuration called dispersed structure (Fig. 2.4b).

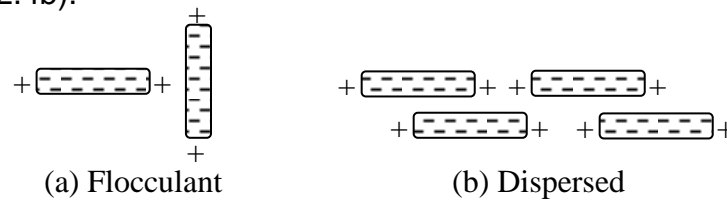


Fig. 2.4 Different arrangement of clay particle

A lot of micro and macro level behaviour of clays are associated with these arrangement of clay particles (Mitchell and Soga 2005).

## Swelling and shrinkage

Some clay minerals when exposed to moisture are subjected to excessive swelling and during drying undergo excessive shrinkage. A lot of engineering properties of soil is affected by this behaviour and the stability of structures founded on such soils become detrimental. The swelling of clay minerals decreases in the order montmorillonite > illite > kaolinite.

### 2.1.3 Minerals other than silica and clay

Other than silica and clay, subsurface contains a variety of minerals such as oxides and carbonates that governs the reactivity of soil and its interaction with the environment. Some of the abundant metal oxide minerals present are iron oxides (hematite, magnetite, goethite etc.) and aluminium oxides (gibbsite, boehmite). Other oxide minerals (such as manganese oxides, titanium oxides) are far less than Fe and Al oxides, but because of small size and large surface area, they would affect very significantly the geochemical properties of subsurface. These oxides are mostly present in residual soils of tropical regions. Other major components include soluble calcium carbonate and calcium

sulphate, which has relatively high surface area. In most soils, quartz is the most abundant mineral, with small amount of feldspar and mica present. Carbonate minerals such as calcite and dolomite are found in some soils in the form of bulky particles, precipitates etc. Sulphate minerals mainly gypsum are found in semiarid and arid regions.

#### **2.1.4 Soil mineralogy characterization**

One of the very well established methods for mineralogy characterization of fine-grained soils is by using X-ray diffraction (XRD) analysis. Majority of the soil minerals are crystalline in nature and their structure is defined by a unique geometry. XRD identifies minerals based on this unique crystal structure. In XRD, characteristic X-rays of particular wave length are passed through a crystallographic specimen. When X-ray interacts with crystalline specimen it gives a particular diffraction pattern, which is unique for a mineral with a particular crystal structure. The diffraction pattern of the soil specimen (according to its crystal structure), which is based on powder diffraction or polycrystalline diffraction, is then analyzed for the qualitative and quantitative (not always) assessment of minerals. Sample preparation method for XRD should be done with great care as the XRD reaches only a small layer (nearly 50  $\mu\text{m}$ ) from the surface of the sample. Hence, homogeneity is very important. Soil sample is initially dried and sieved through 2 mm sieve. Sieved sample is homogenized in a tumbler mixer for 30 min. A control mix of 30 g was taken and ground in lots of 15 g in a gyratory pulverizer. 15 percent by weight of  $\text{KIO}_4$  (internal standard) was added to 5 g of specimen and again homogenized in a mixer. The prepared specimen is then subjected to analysis.

X-ray wave of monochromatic radiation ( $K_\alpha$ ) is commonly obtained from copper radiation, which is commonly known as Cu-  $K_\alpha$ . A typical XRD output is represented by Fig. 2.5. It can be noted from the figure that ordinate represent relative intensity of X-ray diffraction and abscissa represents twice of angle at which a striking X-ray beam of wave length  $\lambda$  makes with parallel atomic planes. Based on this diffraction pattern, the minerals can be identified by matching the

peak with the data provided by International Centre Diffraction Data (ICDD) formerly known as Joint Committee on Powder Diffraction Standards (JCPDS).

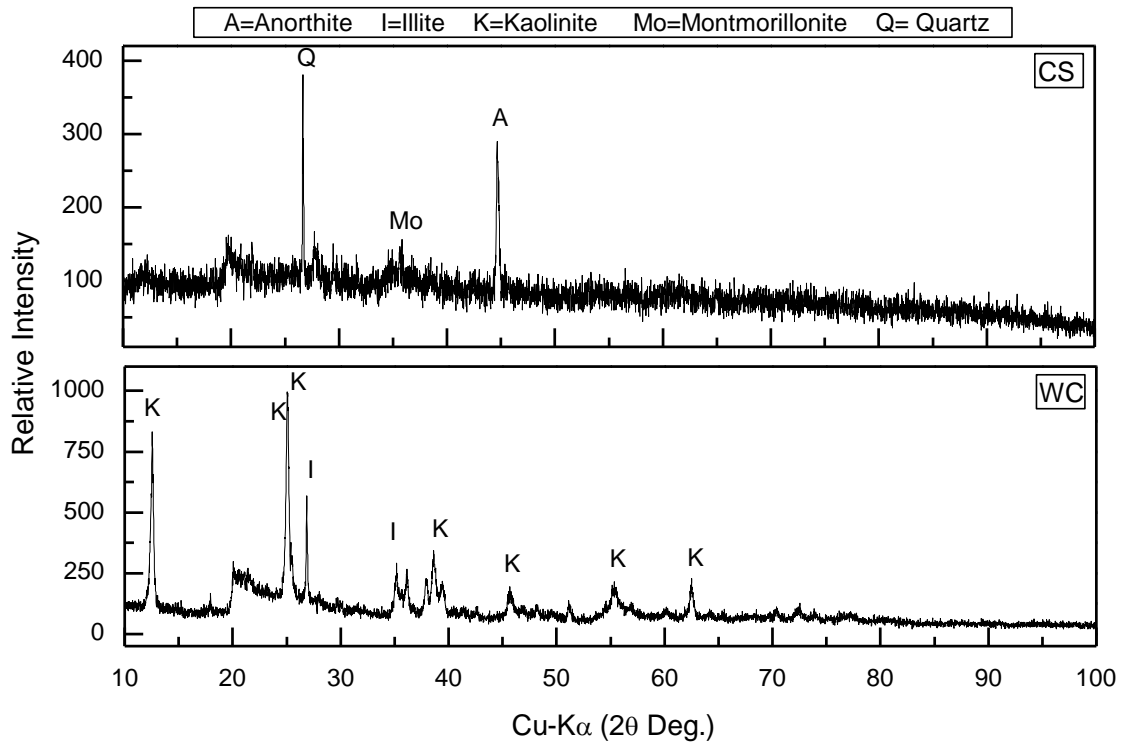


Fig. 2.5 A typical XRD pattern with mineral identification for two different soils (modified from Sreedeeep 2006)

It is understood that the area under the peak of diffraction pattern gives the quantity of each phase present in the specimen. However, quantitative determination of mineral composition in soils based on simple comparison of diffraction peak height under peak is complex and uncertain because of different factors such as mineral crystallinity, hydration, surface texture of the specimen, sample preparation, non-homogeneity of soil samples, particle orientation etc. The method of quantification will be more precise for those soils with less number of minerals. Al-Rawas et al. (2001) have discussed about constant mineral standard method and constant clay method for quantification of clay minerals. In the first method, increasing quantity of clay are added to the fixed mass of known standard and the difference in X-ray diffraction intensity when the specimen changes from 100 percent standard to 100 percent clay is noted. The peak area ratio for each component is then plotted against percentage of clay, based on

which regression equation is determined. This regression equation is further used for mineral quantification. In the second method, known weight of pure standard mineral is added to clay containing the same components, and the change in the reflection peak-area intensity of each component is measured to estimate the weight proportion of that component.

The fundamental discussion on the theory of XRD is quite extensive and cannot be dealt in this course. Interested readers can go through literature available on XRD in detail (Whittig and Allardice 1986; Moore and Reynolds 1997; Chapuis and Pouliot 1996; Manhaes et al. 2002).

### ***2.1.5 Applications of soil mineral analysis in geoenvironmental engineering***

As explained above, the soil-water and soil-water-contaminant interaction and hence reactivity is greatly influenced by the mineralogy.

Chapuis and Pouliot (1996) have demonstrated the use of XRD for determining bentonite content in soil-bentonite liners employed in waste containment. Predicting global hydraulic performance of liner is very difficult with small scale permeability test conducted in the field. There are no methods available for the prediction of global permeability from small scale permeability test. For this purpose, the XRD quantified bentonite content is used for understanding the global hydraulic performance of liners. The soil used in this study was subjected to heating at 550 °C in order to reduce its tendency for hydration, there by eliminating the possibility of variation in diffraction intensity due to difference in hydration. An internal standard was used for controlling X-ray absorption and has been added to all specimens in equal quantity. In this study, authors also indicate the usefulness of using XRD for knowing the quality and constancy of bentonite supplied for the project.

When there are problems associated with expansive soils, the best method for identifying the problem is by conducting XRD and checking for expansive clay minerals. Bain and Griffen (2002) highlights that acidification of soil can be understood by understanding the transformation of minerals. This is

mainly due to the fact that micas get transformed to vermiculite by weathering process under acidic condition. Velde and Peck (2002) have shown that crops can affect the clay mineralogy of the soils on which they are grown over periods of time. The influence of fertilizer addition on cropping can be studied by analyzing transformation of soil mineral in the field where the cropping has been done. By analyzing mineralogy, the land use practices can be assessed.

## 2.2 Soil-water-contaminant interaction

Under normal conditions, water molecules are strongly adsorbed on soil particle surface. Unbalanced force fields are generated at the interface of soil-water, which increases soil-water interaction. When particles are finer, magnitude of these forces are larger than weight of these particles. This is mainly attributed to low weight and high surface area of fine particles. Before discussing the concepts of soil-water interaction, a brief discussion is given on forces between soil solids.

### Forces between soil solids

There are essentially two type of bonding: (1) Electrostatic or primary valence bond and (2) Secondary valence bond. Atoms bonding to atoms forming molecules are termed as primary valence bond. These are intra-molecular bonds. When atoms in one molecule bond to atoms in another molecule (intermolecular bond), secondary valence bonds are formed. What is more important in terms of soil solids is the secondary valence bonds. van der Waals force and hydrogen bonds are the two important secondary valence forces. Secondary valence force existing between molecules is attributed to electrical moments in the individual molecules. When the centre of action of positive charge coincide with negative charge, there is no dipole or electric moment for the system and is termed as non-polar. However, for a neutral molecule there can be cases where the centre of action of positive and negative charge does not coincide, resulting in an electric or dipole moment. The system is then termed as polar. For example, water is dipole. Also, unsymmetrical distribution of electrons in silicate crystals makes it polar. Non-polar molecules can become polar when

placed in an electric field due to slight displacement of electrons and nuclei. This is induced effect and the extent to which this effect occurs in molecule determines its polarisability.

van der Waals force is the force of attraction between all atoms and molecules of matter. This force comes into effect when the particles are sufficiently close to each other. Hydrogen bond is formed when a hydrogen atom is strongly attracted by two other atoms, for example: water molecules. This bond is stronger than Van der Waals force of attraction and cannot be broken under stresses that are normally experienced in soil mechanics. These secondary valence bonds play a vital role in understanding soil-water interactions. Essentially, the forces in soil mechanics may be grouped as gravitational forces and surface forces. From classical soil mechanics perspective, gravitational forces which are proportional to mass are more important. However, in geoenvironmental engineering surface forces are important. Surface forces are classified as attractive and repulsive forces. Attractive forces include (a) Van der Waals London forces (b) hydrogen bond (c) cation linkage (d) dipole cation linkage (e) water dipole linkage and (f) ionic bond. Van der Waals London force is the most important in soils and becomes active when soil particles are sufficiently close to each other. For example, fine soil particles adhere to each other when dry. Cation linkage acts between two negatively charged particles as in the case of illite mineral structure. Other types of forces are less important and will not be explained in this section. Repulsive forces include like charge particle repulsion and cation-cation repulsion.

### **2.2.1 Soil-water interaction**

Water present in pore spaces of soil is termed as soil water or pore water. The quantity of water present in the pores will significantly influence its physical, chemical and engineering properties. It can be classified as (a) free water or gravitational water and (b) held water or environmental water. As the name suggests, free water flows freely under gravity under some hydraulic gradient and are free from the surface forces exerted by the soil particle. This water can

be removed easily from the soil. Environmental water is held under the influence of surface forces such as electrochemical forces or other physical forces. Both type of water are important in geoenvironmental engineering. There are many cases like seepage and infiltration problems whose solution necessitates the knowledge of free water. However, these concepts are discussed in detail in classical soil mechanics text books. At the same time, there are several phenomena, which will be discussed in detail in this course, where the understanding of held water becomes essential. The mechanism of soil-held water interaction is complex and influenced by soil type, mineralogy, current and past environmental conditions, stress history etc.

Held water can be further subdivided into structural water, adsorbed water and capillary water. Structural water is present within the crystal structure of mineral. This water is not very important as far as engineering property of soil is concerned. For finding solution to several problems in geoenvironmental engineering, it is essential to understand in detail adsorbed water and capillary water.

### **Adsorbed water**

Adsorbed water is strongly attracted to soil mineral surfaces especially clays. Dry soil mass can adsorb water from atmosphere even at low relative humidity and it is known by the name hygroscopic water content. For the same soil, hygroscopic water content will vary depending on relative humidity and temperature. Adsorptive forces between soil and water is polar bond and depends on specific surface area of soil. Adsorbed water or bound water behaves differently from the normal pore water. It is immobile to normal hydrodynamic forces and its density, freezing point etc. are different from free water.

Possible mechanisms for water adsorption (Low 1961)

a) Hydrogen bond and dipole attraction: Soil minerals are essentially made up of oxygen or hydroxyls, facilitating easy formation of hydrogen bonds. Surface

oxygen can attract positive corner of water molecules ( $H^+$ ) and  $H^+$  present in  $OH^-$  can attract negative corner ( $O^{2-}$ ) of water molecules as depicted in Fig. 2.6.

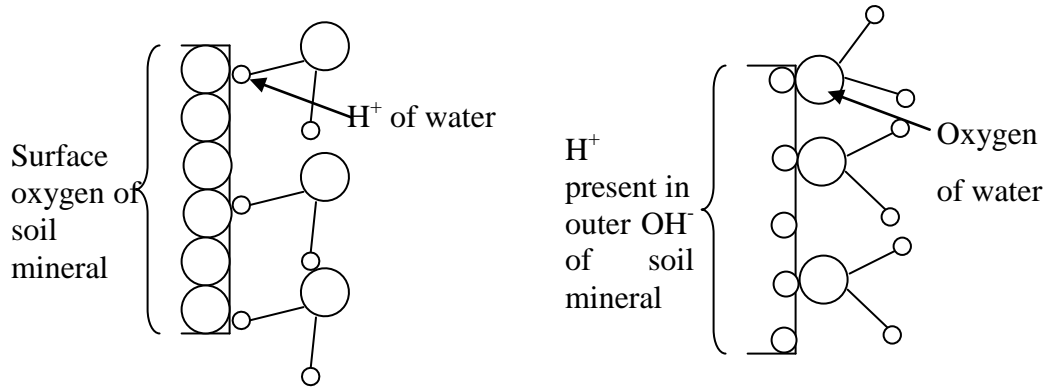


Fig. 2.6 Water adsorption by hydrogen bond in soil minerals

b) Hydration of cations: Every charged soil surface has affinity towards ions, specifically cations. These cations get hydrated by water dipole due to the formation of hydrogen bond as shown in Fig. 2.7. Therefore, cations present in the soil would contribute to the adsorbed water. In dry clays, these cations occupy in the porous space of clay mineral. During hydration, these cations engulf with water molecules and move towards centre space between two clay particles. The discussion on hydration of cations is very vast and its significance will be dealt in detail, after this section.

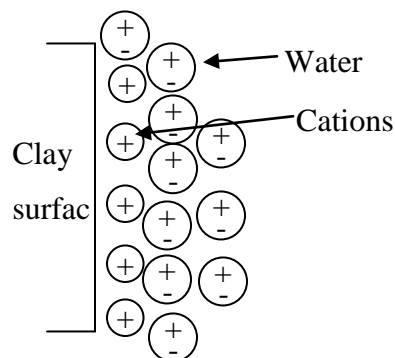


Fig. 2.7 Water adsorption by ion hydration



b) Osmosis: Concentration of cations increases with proximity to clay surface. The relatively high concentration would induce osmotic flow of water to neutralize the high concentration of cations. Such an osmotic phenomenon is true in the case of clays which act as semi-permeable membranes (Fritz and Marine 1983).

c) Attraction by Van der Waals-London forces causes attraction of water molecules towards clay surface.

d) Capillary condensation: A range of pore size is possible in soils due to the different particle size distribution and packing density. For saturation less than 100 percent, water and water vapour can get retained in soil pores by capillary forces and attraction to particle surfaces.

### **Properties of adsorbed water**

Several studies have been conducted to understand structural, chemical, thermodynamic and mechanical properties of soil water by using different techniques such as X-ray diffraction, density measurements, dielectric measurement, nuclear magnetic resonance etc.

Density: At low water content, less than that needed to form three layers on clay surfaces, the density of adsorbed water is greater than that for normal water. For higher water content the density variation with reference to free water is less.

Viscosity: There is not much difference in viscosity between adsorbed and free water. This is a very important observation relative to analysis of seepage, consolidation etc. for unsaturated soils.

Dielectric constant: Dielectric property of a material depends on the ease with which the molecules in the material can be polarized. It is observed that dielectric constant of adsorbed water is less (50) as against 80 for free water.

Freezing of adsorbed water: Adsorbed water exhibit freezing point depression as compared to free water. This is mostly attributed to the less molecular order of adsorbed water as compared to free water.

Other properties: Energy is released when water is adsorbed by clay surface. There is a time-dependent increase in moisture tension of water after mechanical disturbance of at-rest structure of clay-water. The thermodynamic, hydrodynamic

and spectroscopic properties of adsorbed water vary exponentially with distance from particle surface. The surface interaction effect is evident to a distance of 10 nm from the surface. This corresponds to around 800 percent water content in smectite and 15 percent in kaolinite (Mitchell and Soga 2005).

### **Diffused double layer (DDL)**

Diffused double layer (DDL) is the result of clay-water-electrolyte interaction. Cations are held strongly on the negatively charged surface of dry fine-grained soil or clays. These cations are termed as adsorbed cations. Those cations in excess of those needed to neutralize electronegativity of clay particles and associated anions are present as salt precipitates. When dry clays come in contact with water, the precipitates can go into solution. The adsorbed cations would try to diffuse away from the clay surface and tries to equalize the concentration throughout pore water. However, this movement of adsorbed cations are restricted or rather minimized by the negative surface charge of clays. The diffusion tendency of adsorbed cations and electrostatic attraction together would result in cation distribution adjacent to each clay particle in suspension. Fig. 2.8 presents such a distribution of ions adjacent to a single clay particle. The charged clay surface and the distributed ions adjacent to it are together termed as diffuse double layer (DDL). Close to the surface there is high concentration of ions which decreases outwards. Thus there are double layers of ions (a) compressed layer and (b) diffused layer and hence the name double layer. The variation in concentration of cations and anions in pore water with distance from clay surface is also presented in Fig. 2.8. A high concentration of cations close to clay surface gradually reduces, and reaches equilibrium concentration at a distance away from clay surface. For anions, concentration increases with distance from clay surface.

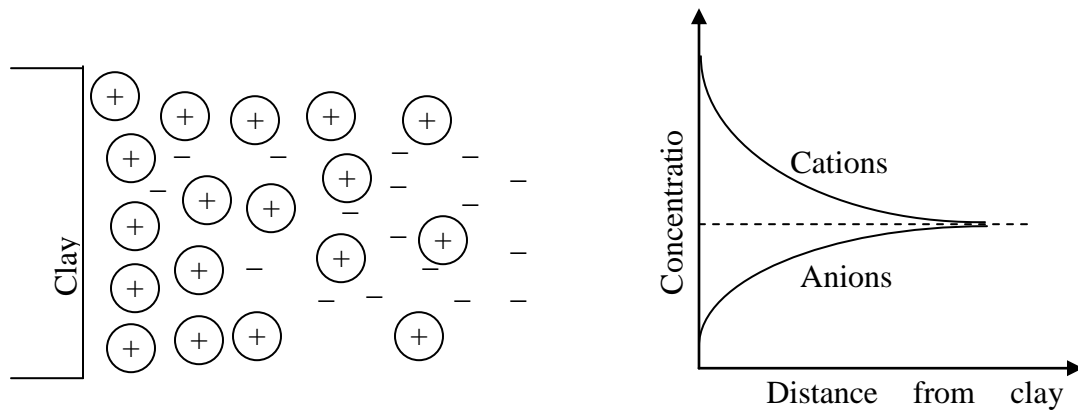


Fig. 2.8 Distribution of ions adjacent to clay surface (modified from Mitchell and Soga 2005)

Several theories have been proposed for defining ion distribution in DDL. Gouy and Chapman is one of the initial explanations on DDL ion distribution (Mitchell and Soga 2005). The theory has been further modified by Derjaguin and Landau; Verwey and Overbeek which is known by the name DLVO theory (Mitchell and Soga 2005). In addition to ion quantification, DLVO describe the repulsive energies and forces of interaction between clay particles and prediction of clay suspension stability. Sposito (1989) observed that the theory predicts ion distribution reasonably for only smectite particles suspended in monovalent ion solution at low concentration. However, the theory can still be used for defining forces of interaction, flocculation, dispersion, clay swelling etc. A much more refined description of interparticle forces has been proposed by Langmuir (1938) and extended by Sogami and Ise (1984).

Following are the assumptions which pertain to the formulation of DDL theory:

- a) Ions in the double layer are point charges and there are no interactions among them.
- b) Charge on particle surface is uniformly distributed.
- c) Clay particle surface is large relative to the thickness of double layer (to maintain one dimensional condition).

d) Permittivity of medium adjacent to particle surface is independent of position.

Permittivity is the measure of the ease with which a molecule can be polarized and oriented in an electric field.

Concentration of ions (no of ions/m<sup>3</sup>) of type i,  $n_i$ , in force field at equilibrium is given by Boltzmann equation as follows:

$$n_i = n_{i0} \exp\left(\frac{E_{i0} - E_i}{kT}\right) \quad (2.1)$$

$E$  is the potential energy,  $T$  is the temperature in Kelvin,  $k$  is the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K), subscript 0 represents reference state which is at a large distance from the surface.

Potential energy of an ion “i” in electric field is given by Eq. 2.2.

$$E_i = v_i e \psi \quad (2.2)$$

where  $v_i$  is the ionic valence,  $e$  is the electronic charge ( $=1.602 \times 10^{-19}$  C) and  $\psi$  is the electrical potential at a point.  $\psi$  is defined as the work done to bring a positive unit charge from a reference state to the specified point in the electric field. Potential at the surface is denoted as  $\psi_0$ .  $\psi$  is mostly negative for soils because of the negative surface charge. As distance from charged surface increases,  $\psi$  decreases from  $\psi_0$  to a negligible value close to reference state. Since  $\psi = 0$  close to reference state,  $E_{i0} = 0$ .

Therefore,  $E_{i0} - E_i = -v_i e \psi$  and Eq. 2.1 can be re-written as

$$n_i = n_{i0} \exp\left(\frac{-v_i e \psi}{kT}\right) \quad (2.3)$$

Eq. 2.3 relates ion concentration to potential as shown in Fig. 2.9.

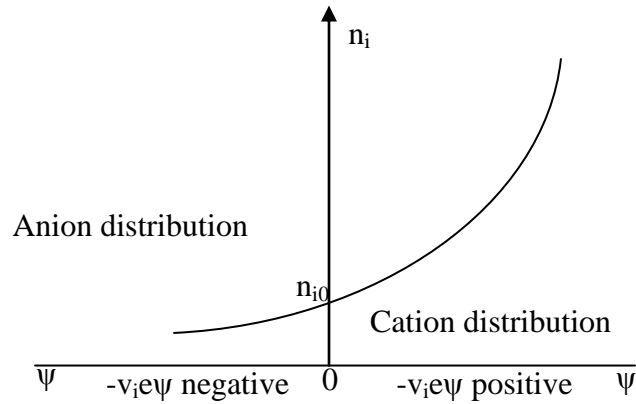


Fig. 2.9 Ion concentration in a potential field (modified from Mitchell and Soga 2005)

In Fig. 2.9 anion distribution is marked negative due to the reason that  $v_i$  and  $\psi$  are negative and hence  $-v_i e \psi$  will be negative. For cations,  $v_i$  is positive and  $\psi$  is negative and hence  $-v_i e \psi$  will be positive. For negatively charged clay surface,  $n_{i,cations} > n_{i0}$  and  $n_{i,anions} < n_{i0}$ .

One dimensional Poisson equation (Eq. 2.4) relates electrical potential  $\psi$ , charge density  $\rho$  in  $C/m^3$  and distance ( $x$ ).  $\epsilon$  is the static permittivity of the medium ( $C^2 J^{-1} m^{-1}$  or  $Fm^{-1}$ ).

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho}{\epsilon} \quad (2.4)$$

$$\rho = e \sum v_i n_i = e(v_+ n_{+} - v_- n_{-}) \quad (2.5)$$

$n_i$  is expressed as ions per unit volume, + and – subscript indicates cation and anion.

Substituting Eq. 2.3 in 2.5

$$\rho = e \sum v_i n_{i0} \exp\left(\frac{-v_i e \psi}{kT}\right) \quad (2.6)$$

Hence, 
$$\frac{d^2 \psi}{dx^2} = -\frac{e}{\epsilon} \sum v_i n_{i0} \exp\left(\frac{-v_i e \psi}{kT}\right) \quad (2.7)$$

Eq. 2.7 represents differential equation for the electrical double layer adjacent to a planar surface. This equation is valid for constant surface charge. Solution of

this differential equation is useful for computation of electrical potential and ion concentration as a function of distance from the surface.

### Different models representing double layer (Yong 2001)

A) Helmholtz double layer: This model follows the simplest approximation that surface charge of clays are neutralized by opposite sign counter ions placed at a distance of “d” away from the surface. The surface charge potential decreases with distance away from the surface as shown in Fig. 2.10.

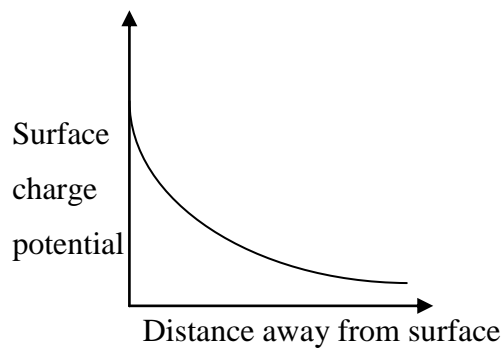


Fig. 2.10 Variation of surface charge potential with distance from clay surface (modified from Mitchell and Soga 2005)

In this model, double layer is represented by negatively and positively charged sheets of equal magnitude (Yong 2001). In this model, positive charges are considered to be stationary, which is against the reality that cations are mobile. It is opined that this model is too simple to address the real complexities of double layer.

B) Gouy Chapman model: Gouy suggested that interfacial potential at the charged surface can be attributed to the presence of a number of ions of given sign attached to the surface and to an equal number of opposite charge in the solution. The counter ions tend to diffuse into the liquid phase, until the counter potential set up by their departure restricts its diffusion. The kinetic energy of counter ions affects the thickness of resulting double layer. Gouy and Chapman proposed theoretical expression for electric potential in double layer by combining Boltzman equation (2.1) and Poisson equation (2.4), where in Eq. 2.1 relates ion distribution to electric potential and Eq. 2.4 relates electric potential and distance (Reddi and Inyang, 2000). This combination is given by Eq. 2.7. For

the case of a single cation and anion species of equal valency ( $i=2$ ) and  $n_0 = n_0^+ = n_0^-$  and  $v^+ = v^- = v$ , then Eq. 2.7 simplifies to Poisson-Boltzmann equation (Eq. 2.8).

$$\frac{d^2\psi}{dx^2} = \frac{2n_0 ve}{\epsilon} \sinh \frac{ve\psi}{kT} \quad (2.8)$$

Solutions of the above are usually given in terms of the dimensionless quantities as stated below.

$$\left. \begin{aligned} y &= \frac{ve\psi}{kT} \\ z &= \frac{ve\psi_0}{kT} \end{aligned} \right\} \text{Potential functions} \quad (2.9)$$

$$\xi = Kx \quad \text{Distance function} \quad (2.10)$$

$$\text{where } K^2 = \frac{2n_0 e^2 v^2}{\epsilon kT} \text{ or } K = \sqrt{\frac{8\pi e^2 v^2 n_0}{DKT}} \quad (2.11)$$

D is the dielectric constant of the medium. According to Eq. 2.11, K depends on the characteristics of dissolved salt and fluid phase. However, actual values of concentration and potential at any distance from the surface would also depend on surface charge, surface potential, specific surface area and dissolved ion interaction. This means that the type of clays and pore solution are very important.

Solution can be obtained for a set of boundary conditions, one at the surface and other at infinite distance:

$$y = 0 \text{ and } \frac{dy}{d\xi} = 0 \text{ at } \xi = \infty \text{ and } y = z = \frac{ve\psi_0}{kT} \text{ at } \xi = 0$$

$\psi_0$  is the potential at the clay surface.

$$\text{For } z \ll 1, \psi = \psi_0 e^{-Kx}$$

$$(2.12)$$

$$\text{For } z = \infty, \psi = \frac{2kT}{e} \ln \coth \frac{Kx}{2} \quad (2.13)$$

For some arbitrary  $z$  and  $\xi \gg 1$ ,  $\psi = \frac{4kT}{e} \left( \frac{e^{z/2} - 1}{e^{z/2} + 1} \right) e^{-\xi}$

(2.14)

Eq. 2.12 is commonly referred to as Debye-Huckel equation and  $1/K$  represents characteristic length or thickness of double layer (Mitchell and Soga 2005). Knowing electric potential from above equations, it is possible to determine ion distribution from Eq. 2.3.

For cations:  $n_+ = n_{i0} \exp\left(\frac{-v_i e \psi}{kT}\right)$

(2.15)

For anions:  $n_- = n_{i0} \exp\left(\frac{v_i e \psi}{kT}\right)$  (2.16)

This model is accurate only if the soil behaves like a true parallel plate system. It does not satisfactorily provide description of  $\psi$  immediately adjacent to the charged particle. This is mainly due to the mechanisms associated with chemical bonding and complexation. Gouy-Chapman model is ideally suited for qualitative comparisons. The basic assumption in Boltzmann equation where the potential energy is equated to the work done in bringing the ion from bulk solution to some point, does not consider other interaction energy components.

### C) Stern model

According to Stern model total cations required to balance the net negative charge on clay surface consists of two layers. The first layer is of cations adsorbed on to the clay surface and are located within a distance of  $\delta$ . The clay surface charges and the adsorbed group of cations are termed as electric double layer (EDL) or Stern layer. The other group of cations are diffused in a cloud surrounding the particle and can be described by Boltzmann distribution as discussed in the previous section. The total surface charge ( $\sigma_s$ ) is counter balanced by Stern layer charge  $\sigma_\delta$  and diffuse layer charge  $\sigma_{dl}$ . The surface potential ( $\psi_s$ ) depends on electrolyte concentration and surface charge (whether it is constant or pH dependent). It decreases from  $\psi_s$  to  $\psi_\delta$  when the distance



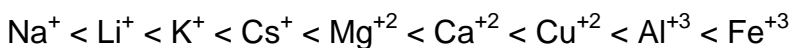
increases from surface to the outer boundary of Stern layer. Beyond this distance,  $\psi$  is quantified by using Eq. 2.13.

There are other DDL models like DLVO which deals with complex interactions. However, these are not discussed in this course. The interested readers can refer to Yong (2001) for further reading.

## Cation exchange capacity

From previous discussion, it is clear that clay surface adsorbs specific amount and type of cations under a given environmental conditions such as temperature, pressure, pH and pore water chemistry. The adsorbed cations can get partly or fully replaced by ions of another type subject to changes in the environmental condition. Such changes can alter the physico-chemical characteristics of soil. The most common cations present in the soil are sodium, potassium, calcium and magnesium. Marine clays and saline soils contain sodium as the dominant adsorbed cation. Acidic soils contain  $Al^{+3}$  and  $H^+$ . The most common anions are sulphate, chloride, phosphate and nitrate.

Cation exchange capacity (CEC) is defined as the sum of exchangeable cations soil can adsorb per 100 g of dry soil. Its unit is meq./100 g and normally its value ranges between 1 and 150 meq./100 g. The value represents the amount of exchangeable cations that can be replaced easily by another incoming cation. The replaceability of cations depends on valency, relative abundance of different ion type and ion size. All other factors remaining same, trivalent cations are held more tightly than divalent and univalent ions. A small ion tends to replace large ions. It is also possible to replace a high replacing power cation by one of low replacing power due to the high concentration of latter in the pore solution. For example,  $Al^{+3}$  can be replaced by  $Na^+$  due to its abundance. A typical replaceability series is given as follows: (Mitchell and Soga 2005)



The rate of exchange reaction would essentially depend on clay type, pore solution concentration, temperature, pH etc. In kaolinite, the reaction takes place quickly. In illite, a small part of the exchange sites may be between unit layers of

minerals and hence would take more time. In smectite minerals, much longer time is required because the major part of exchange capacity is located in the interlayer region.

For a pore solution containing both monovalent and divalent cations, the ratio of divalent to monovalent cations is much higher in adsorbed layer than in the equilibrium solution. If M and N represent monovalent cation concentrations, P the concentration of divalent ions, subscript s and e represent adsorbed ions on soil and that in equilibrium solution, respectively, then

$$\left(\frac{M^+}{N^+}\right)_s = k_1 \left(\frac{M^+}{N^+}\right)_e \quad (2.17)$$

$$\left(\frac{M^+}{P^{2+}}\right)_s = k_2 \left(\frac{M^+}{(P^{2+})^{\frac{1}{2}}}\right)_e \quad (2.18)$$

where  $k_1$  and  $k_2$  are selectivity constants, which can be obtained experimentally. Following, Eq. 2.18 it can be further written as

$$\left(\frac{Na^+}{Ca^{2+} + Mg^{2+}}\right)_s = k \left(\frac{Na^+}{\left(\frac{Ca^{2+} + Mg^{2+}}{2}\right)^{\frac{1}{2}}}\right)_e \quad (2.19)$$

The concentration of cation is in milliequivalents per litre. The quantity

$$\left(\frac{Na^+}{\left(\frac{Ca^{2+} + Mg^{2+}}{2}\right)^{\frac{1}{2}}}\right)_e$$

is termed as sodium adsorption ratio (SAR) in  $(\text{meq./litre})^{1/2}$ . If

the composition of pore fluid and  $k$  is known, the relative amounts of single and divalent cations in the adsorbed cation complex can be determined. The details of selectivity constants for a wide variety of clays are reported by Bruggenwert and Kamphorst (1979). Sodium present in the adsorbed layer is normalized with respect to total exchange capacity as represented by Eq. 2.20 and is termed as exchangeable sodium percentage (ESP).

$$\text{ESP} = \left( \frac{(\text{Na}^+)_s}{\text{total exchange capacity}} \right) \times 100$$

(2.20)

ESP and SAR are considered to be a reliable indicator of clay stability against breakdown and particle dispersion especially for non-marine clays (Mitchell and Soga 2005). Clays with ESP > 2 percent is considered as dispersive.

Other quantitative attributes of cation exchange in soils is the property known as “the percentage base saturation” (Eq. 2.21), which denotes the measure of the proportion of exchangeable base on the soil exchange complex.

$$\text{Base saturation (\%)} = \frac{\text{Ca}^{+2} + \text{Mg}^{+2} + \text{K}^+ + \text{Na}^+}{\text{CEC}} \times 100 \quad (2.21)$$

## Factors influencing CEC of the soil

### a. pH of the soil

It is observed that CEC of the soil increases with an increase in pH. Therefore, it is recommended to maintain a neutral pH (= 7.0) for determining CEC of the soil.

### b. Presence of organic matter

The presence of organic carbon in clays reduces its CEC (Syers et al., 1970). However, some studies report an increase in CEC with increasing organic matter contents and this effect was more pronounced in coarser fractions.

### c. Temperature

The ion exchange capacity decreases with an increase in temperature.

### d. Particle size

It is observed that CEC increase with decreasing particle.

### e. Calcium carbonate contents ( $\text{CaCO}_3$ )

Higher amount of  $\text{CaCO}_3$  in soil leads to higher CEC.

### f. Mineralogy

Active clay minerals increase CEC of the soil.

## Determination of CEC by Ammonium replacement method

Horneck et al. (1989) have proposed a method for determining the CEC of soils by using ammonium replacement technique. This method involves saturation of the cation exchange sites on the soil surface with ammonium, equilibration, and removal of excess ammonium with ethanol, replacement and leaching of exchangeable ammonium with protons from HCl acid. It must be noted that this method is less suited for soils containing carbonates, vermiculite, gypsum and zeolite minerals. The procedure is discussed as follows:

Take about 10 g of soil, in 125 ml flask, add 50 ml of ammonium acetate solution and place the flask in reciprocating shaker for 30min. The shaking process is repeated with blank solution as well.

1 liter vacuum extraction flask is connected to a funnel with Whatman no.5 filter paper. The soil sample is then transferred to the funnel and leached with 175 ml of 1 N ammonium acetate. The leached solution is analyzed for extractable K, Ca, Mg, and Na.

The soil sample in the funnel is further leached with ethanol and the leachate is discarded.

Transfer the soil to a 500 ml suction flask and leach the soil sample with 225 ml of 0.1N HCl to replace the exchangeable ammonium. Make up the leachate to a final volume of 250ml in a standard flask using deionized water.

The concentration of ammonium in the final leachate is measured, and CEC is calculated using Eq. 2.22.

$$\text{CEC (meq./100g of soil)} = \left( \text{ammonium concentration} \times \frac{0.25}{14} \times \frac{100}{\text{sample size(g)}} \right)$$

(2.22)

IS code (IS 2720, Part 24 1976) and USEPA (EPA SW-846) also provides alternate methods for determining CEC of the soil. The range of CEC values for different soil minerals are listed in Table 2.3 (Caroll 1959). It can be noted that highly active soil minerals such as montmorillonite and vermiculite exhibit high CEC. Therefore, CEC is important in assessing the chemical properties of the soil in terms of its reactivity, contaminant retention mechanism etc.

Table 2.3 CEC values of common soil minerals

Mineral	CEC (meq./100g) at pH 7
Kaolinite	3-15
Illite	10-40
Montmorillonite	70-100
Vermiculite	100-150
Halloysite 2H <sub>2</sub> O	5-10
Halloysite 4H <sub>2</sub> O	40-50
Chlorite	10-40
Allophane	60-70

### Quantification of soil water

One of the main attributes that makes soil mechanics different from solid mechanics is the presence of water in the void spaces. The quality and quantity of water will significantly influence physical, chemical and engineering properties of soil such as plasticity, permeability, water retention, mass transport etc. The water present in the soil voids are quantified as water content, which is also referred to as capacity factor. Energy status of water is called intensity factor. Water content is further divided into gravimetric and volumetric water content. When water content is defined as the ratio of weight of water to the weight of soil solids (weight basis) it is termed as gravimetric water content, denoted as “w”. Volumetric water content is expressed as the ratio of volume of water ( $V_w$ ) to the total volume of soil ( $V$ ) and denoted by  $\theta$ .

$$\theta = V_w/V \quad (2.23)$$

$$\begin{aligned} &= W_w/\gamma_w \times 1/V \\ &= W_w/\gamma_w \times (W_d/W_d) \times 1/V \end{aligned}$$

$$W_d/V = \gamma_d$$

$$W_w/W_d = w$$

$$\theta = w \times (\gamma_d/\gamma_w) \quad (2.24)$$

$$\begin{aligned} \text{Also, } \theta &= w \times (G \gamma_w/(1+e))/\gamma_w \\ &= w \times ((S_r \times e)/w) \times 1/(1+e) \\ &= e/(1+e) \times S_r \end{aligned}$$

$$= n \times S_r \quad (2.25)$$

Where  $W_w$  is the weight of water,  $\gamma_w$  is the unit weight of water,  $W_d$  is the weight of dry soil,  $\gamma_d$  is the dry unit weight of soil,  $G$  is the specific gravity of soil,  $e$  is the void ratio,  $n$  is the porosity and  $S_r$  is the degree of saturation. Eqs. 2.24 and 2.25 relates  $\theta$  with  $w$  and  $S_r$ , respectively. For a fully saturated soil,  $S_r = 1$  and hence  $\theta$  becomes equal to  $n$ .

There are some dimensionless expressions for water content, which are important for different modelling application. Some of the important expressions are given by Eqs. 2.26 and 2.27.

$$\text{Relative water content, } \theta_{rel} = \theta / \theta_{sat} \quad (2.26)$$

$$\text{Reduced or effective water content, } S_e = (\theta - \theta_r) / (\theta_{sat} - \theta_r) \quad (2.27)$$

Where  $\theta_{sat}$  and  $\theta_r$  are saturated volumetric water content and residual water content. The same expressions are valid in terms of gravimetric water content also.

## Mechanical energy of water

Kinetic energy (KE) of water present in porous media is considered to be negligible due to the low flow velocity in moderate and low permeable soil. However, KE is important in granular soils where velocity is significant and also in the case of preferential flow in soils. Preferential flow is caused in soils due to the formation of macrocracks which is mostly attributed to the shrinkage cracks in soil, holes or burrows created by animals, cracks caused by the roots of plants etc. Water would find an easy path through these cracks and hence known as preferential path ways.

Potential energy (PE) is the most important energy component of water present in the porous media. It is the difference in PE between two spatial locations in soil that determines rate and direction of flow of water. The rate of decrease in PE is termed as hydraulic gradient ( $i$ ). PE of water is termed as soil-water potential. The total soil-water potential ( $\psi_t$ ) is the summation of different PE components as given by Eq. 2.28.

$$\psi_t = \psi_g + \psi_m + \psi_p + \psi_o \quad (2.28)$$

Where  $\psi_g$  is the gravitational potential,  $\psi_m$  is the matric potential,  $\psi_p$  is the pressure potential and  $\psi_o$  is the osmotic potential.

$\psi_g$  is due to the difference in elevation between two reference points and hence it is also known as elevation head ( $z$ ). For this a reference datum position is always defined from which elevation is measured. The point above the datum is negative, and below is positive.  $\psi_m$  is caused due to the adsorptive and capillary forces present in the soil. Such a force always retains water towards the soil surface and hence the potential is always taken as negative.  $\psi_p$  is the pressure potential below the ground water table and hence the potential is always positive. It is the head indicated by a piezometer inserted in the soil and hence it is termed as piezometric head. Such a potential is valid for fully saturated state of the soil. However, saturation due to capillary rise is not considered since such water is held under tension.  $\psi_o$  is caused due to salts and contaminants (solutes) present in the soil pore water. Since the solute present in the water try to retain water molecules,  $\psi_o$  is negative.

In the absence of solutes,  $\psi_m$  can be expressed as follows (Scott 2000):

$$\psi_m = \frac{RT}{M} \ln \frac{e}{e_0} \quad (2.29)$$

Where  $R$  is the universal gas constant (8.314 J/K.mol),  $T$  is the temperature in Kelvin,  $M$  is the mass of a mole of water in kg (0.018015),  $\psi_m$  is in J/kg,  $e$  is the vapour pressure of soil pore water,  $e_0$  is the vapour pressure of pure water at the same temperature.  $e$  is less than  $e_0$  due to the attraction pore water on soil solids. The term  $e/e_0$  is relative vapour pressure.

**Problem:** Relative vapour pressure at 20 °C is 0.85. Calculate  $\psi_m$ . If relative vapour pressure becomes 0.989 then what happens to  $\psi_m$ .

$$\psi_m = \frac{8.314 \times 293}{0.018} \ln 0.85$$

$$= -21989 \text{ J/kg}$$

When relative vapour pressure is 0.989, then  $\psi_m = -1496 \text{ J/kg}$ .

A higher relative vapour pressure is associated with high water content of the soil sample. From this example, it can be noted that as water content increases, matric suction reduces.

Solutes present in soil water results in  $\psi_o$  due to the semi-permeable membrane effect produced by plant roots, air-water inter phase and clays. As concentration of solute increases,  $\psi_o$  also increases.

According to Vant-Hoff's equation,  $\psi_o = RTC_s$  (2.30)

Where  $\psi_o$  is in J/kg,  $C_s$  is the concentration in mol/m<sup>3</sup>, R and T as defined earlier.

According to US Salinity laboratory,  $\psi_o = -0.056 \text{ TDS}$  (2.31)

Where TDS is the total dissolved solids of soil pore water in mg/L and  $\psi_o$  is in kPa.

Also,  $\psi_o = -36 \text{ EC}$  (2.32)

Where EC is the electrical conductivity of soil pore water in dS/m and  $\psi_o$  is in kPa.

$\psi_o$  can also be expressed as  $\frac{RT\rho_w}{M} \ln \frac{e}{e_0}$

(2.33)

where  $\rho_w$  is the density of water in kg/m<sup>3</sup>, M is the mass of one mole of water (kg/mol), R and T as defined earlier, e is the equilibrium vapour pressure of soil pore water containing solutes,  $e_0$  is the vapour pressure of pure water in the absence of solute, and  $\psi_o$  is in kPa.

**Problem:** Calculate total potential of a saturated soil at 20<sup>0</sup>C at a point through which reference datum passes. Saturated volumetric water content is 0.5. 1cm<sup>3</sup> of soil at reference datum has 3x10<sup>-4</sup> moles of solute. Water table is 1.2 m above reference datum.

Total potential  $\psi_t = \psi_g + \psi_p + \psi_m + \psi_o$

$\psi_g = 0$  (at reference datum)

$\psi_m = 0$  (soil is saturated)

$\psi_o = -RTC_s$

$C_s$  is moles/m<sup>3</sup> in pore water



Therefore we need to find the volume of pore water.

Given,  $\theta_{sat} = 0.5 = V_w/V$

$V_w = 0.5 \times 1 \times 10^{-6} \text{ m}^3$

1cm<sup>3</sup> of soil mass will have  $C_s = 3 \times 10^{-4} / 0.5 \times 10^{-6}$

Thus  $\psi_o = -[8.31 \times 293 \times (3 \times 10^{-4} / 0.5 \times 10^{-6})]$

$= -1.46 \times 10^6 \text{ J/kg}$

1J/kg = 10<sup>-6</sup> kPa

$\psi_o = 1.46 \times 10^6 \text{ J/kg} = -1.46 \text{ kPa}$

$\psi_p = 1.2 \times 9.8 = 11.8 \text{ kPa}$

$\psi_t = \psi_p + \psi_o$

$\psi_t = 10.34 \text{ kPa}$

Note: It is important to put the sign for each of the potential.

**Movement of water:** Soil water moves from higher  $\psi_t$  to lower  $\psi_t$ . If we are concerned only about liquid flow, then the contribution of  $\psi_o$  is considered negligible because the solutes also move along with the flowing water. While considering flow of water,  $\psi_t$  can be rewritten as  $\psi_g + \psi_p + \psi_m$ . This total potential is termed as hydraulic potential causing flow. Under hydraulic equilibrium,  $\psi_t$  is same everywhere, spatially.

**Problem:** A soil has a perched water table above a clay horizon situated at a depth of 40 cm from ground surface. Height of water ponded above clay layer is 8 cm. Determine the vertical distribution of  $\psi_t$  at 10 cm interval upto 50 cm depth. Assume conditions of hydraulic equilibrium. Take reference datum at (a) ground surface (b) at water table. Distance downwards is taken -ve.

The solution to this problem is given in table below. Depth is Z. All potential of water is expressed in cm.  $\psi_o$  is not considered.

(a) Reference datum at ground surface

Z (cm)	$\psi_g$	$\psi_o$	$\psi_p$	$\psi_m$	$\psi_t$
--------	----------	----------	----------	----------	----------

0	0	0	0	-32	-32
10	-10	0	0	-22	-32
20	-20	0	0	-12	-32
30	-30	0	0	-2	-32
40	-40	0	8	0	-32
50	-50	0	18	0	-32

$\psi_g$  is the distance of the point from the reference datum. Since it is downwards it is -ve. Since, there is no mention of contamination  $\psi_o$  is taken as zero at all points.  $\psi_p$  occurs only below water table. Water level is at 8 cm above 40 cm depth. Therefore, at 40 cm the  $\psi_p$  will be 8 cm. At 30 cm its value will be zero since it is above water table. At 50 cm, the total height of water is 18 cm. Now the value of  $\psi_m$  is not known. But we know that below water table its value will be zero. Therefore, at 40 cm and 50 cm its value is 0. Therefore, the total potential ( $\psi_t$ ) is known at 40 and 50 cm. It is the algebraic sum of all the water potentials. Therefore, it must be noted here that sign of the potential is very important.  $\psi_t$  at 40 cm and 50 cm is obtained as -32 cm. Since it is under hydraulic equilibrium (given),  $\psi_t$  at all the points have to be -32 cm. Once  $\psi_t$  at all the points are know, then  $\psi_m$  at all locations can be determined. For example, at 10 cm depth,  $\psi_m = [\psi_t - (\psi_g + \psi_m + \psi_p + \psi_o)]$  will give  $-32 + 10 = -22$  cm.

(a) Reference datum at water table

Z (cm)	$\psi_g$	$\psi_o$	$\psi_p$	$\psi_m$	$\psi_t$
0	32	0	0	-32	0
10	22	0	0	-22	0
20	12	0	0	-12	0
30	2	0	0	-2	0
40	-8	0	8	0	0
50	-18	0	18	0	0

With the change in reference datum,  $\psi_g$  also changes. Due to this change,  $\psi_t$  also changes. The method of obtaining other potential remains same as in the previous case.

**Problem:** Assume water is evaporated from top soil and the matric potential is given for depth at 10 cm interval upto 50 cm. Water table is at a large depth greater than 50 cm. Determine total potential and direction of flow. Head is measured in cm. Distance downwards is taken negative. Reference datum is taken as ground surface.

Z (cm)	$\psi_m$	$\psi_g$	$\psi_o$	$\psi_p$	$\psi_t$
0	-1200	-0	0	0	-1200
10	-250	-10	0	0	-260
20	-165	-20	0	0	-185
30	-80	-30	0	0	-110
40	-50	-40	0	0	-90
50	-40	-50	0	0	-90

Since concentration is not mentioned and water table is at a depth larger than problem domain, both  $\psi_o$  and  $\psi_p$  will be zero at all points. Only  $\psi_g$  need to be determined. Between locations at 40 and 50 cm, there will be no flow occurring due to hydraulic equilibrium. From 40 cm depth, movement of water will occur upwards because water potential is low at the ground and high at 40 cm depth. Please note that the magnitude is high at the top (1200) but the potential is negative. This will draw or attract water towards that location.

**Problem:** A 10 cm tile drain with water height 2 cm is placed on clay layer at a depth of 40 cm from ground surface. Find component potential and total potential

at 10 cm interval upto 50 cm depth. Determine the flow direction. Take reference datum at ground surface. Assume matric potential as one half of the distance to top of water table.

Z (cm)	$\psi_g$	$\psi_o$	$\psi_p$	$\psi_m$	$\psi_t$	Flow direction
0	0	0	0	-19	-19	Downward
10	-10	0	0	-14	-24	Downward
20	-20	0	0	-9	-29	Downward
30	-30	0	0	-4	-34	Downward
40	-40	0	2	0	-38	No flow
50	-50	0	12	0	-38	No flow

The above exercise shows that the flow of water takes place towards tile drain from ground surface. This is based on the values of total potential. Flow takes place from higher to lower potential. Please note that sign of the potential is very important.

## Hydrologic horizons

For defining water potential, interaction and movement in soil, it is always convenient to define three hydrologic horizons. These horizons vary in depth and thickness spatially and temporally. One or more of these horizons may be absent as well at a particular place. These three horizons are otherwise termed as zones. These zones are listed as follows and the same is depicted in Fig. 2.11. As depicted in the figure, the boundaries of these horizons have been shown to be horizontal for the sake of convenience. In the field these boundaries may be irregular.

### a) Groundwater zone

This zone is otherwise termed as phreatic zone. This zone exists below ground water table and hence will be fully saturated. Mostly, the saturated soil mechanics is applicable for this zone. Depending upon the factors such as season, rainfall, proximity to water bodies etc. the depth of water table varies and

hence the thickness of phreatic zone. All the voids in this zone are filled with water and water pressure will be always positive.

### **b) Vadoze zone**

The partially saturated zone or unsaturated zone above water table is termed as vadoze zone. This zone extends from the top of the groundwater table to the ground surface. The voids are filled with air or water and the relative percentage is decided by the amount of saturation. The concepts developed for saturated soil mechanics is not applicable for unsaturated zone. Hence, the details of this zone are described in detail in the next section. Lowest portion of this zone can be nearly saturated due to the phenomenon of capillary rise. However, the water in this zone will be held under tension. The capillary height ( $h_c$ ) marked in the Fig. 2.11 is expressed as

$$h_c = \frac{2T\cos\theta}{\rho_w g r} \quad (2.34)$$

T is the surface tension of water,  $\rho_w$  is the density of water, g is the acceleration due to gravity, r is the soil pore radius,  $\theta$  is the contact angle made by water-air interface where it contacts the soil solids.

### **c) Root zone**

This zone corresponds to the top portion of vadoze zone close to ground surface where the plants and trees grow. Moisture dynamics is more in this zone due to the fact that roots draw water and nutrients from the soil. This zone is also subjected to evaporation and evapotranspiration and is in direct interaction with the atmosphere. During precipitation, infiltration and flow of water to the subsurface occurs through this zone.

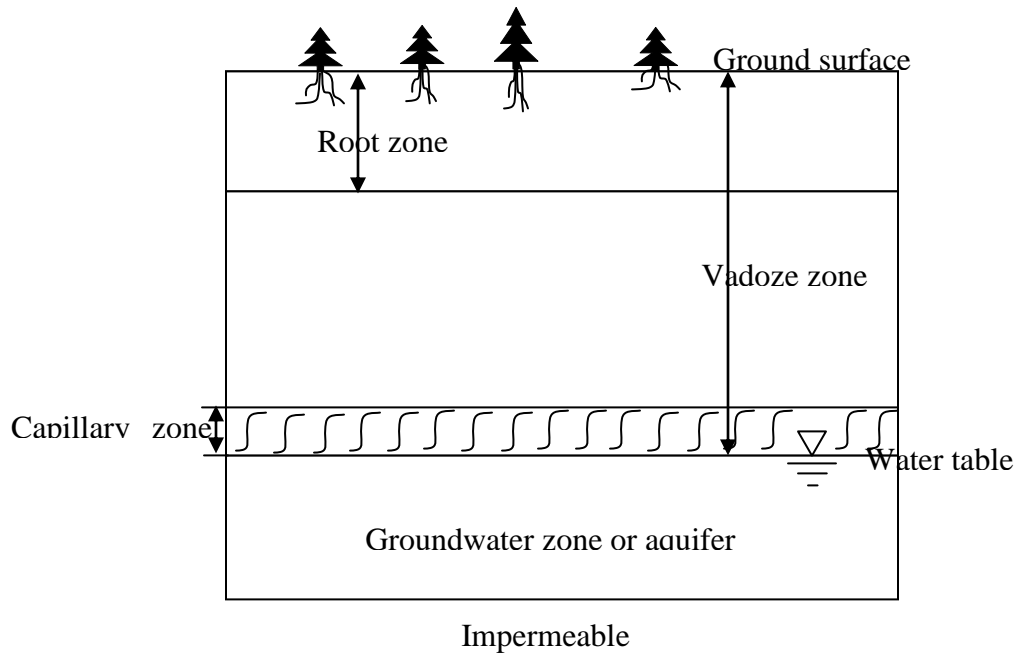


Fig. 2.11 Various hydrologic horizons

### Unsaturated soil (vadoze zone)

Unsaturated soil or partially saturated soil and its behaviour come under the purview of soil-water interaction problem. The classical soil mechanics deals with a two phase system and the concepts are based on the assumption that soil is fully saturated (solid particles and water) or fully dry (solid particles and air). But this assumption may not be valid for some of the real life situations such as highway and railway embankments, airfields, dams, tunnels, natural slopes, linings and covers of waste containment facilities, back fill of retaining walls, stability of vertical excavations, where in soil is generally unsaturated and becomes a three or multiphase system. Therefore, its behaviour does not comply with the concepts developed for saturated soil medium.

The interaction of solid, water and air phase present in the soil develops a complex energy state resulting in negative pore water pressure known as soil suction. Soil suction is defined as the energy required for extracting unit volume of water from soil (Fredlund and Rahardjo 1993). The suction present in the unsaturated soil makes its behaviour highly transient (varies with time) as compared to the steady state behaviour of saturated soils. Therefore, all constant parameters such as water potential, permeability, strength etc. of saturated soil

become a function in unsaturated soil. The study of unsaturated soil behaviour is dependent on the basic relationship between suction and water content (either, gravimetric or volumetric) or saturation. Such a graphical plot as shown in Fig. 2.12 is popularly known as soil-water characteristic curve (SWCC) or water retention characteristic curve (WRCC) in general.

Numerous research works have demonstrated that the WRCC is mandatory for studying the behaviour of unsaturated soil (Fredlund and Rahardjo 1993). For accurate determination of WRCC, the precise measurement of soil suction becomes very important. The major components of soil suction include matric suction ( $\psi_m$ ) and osmotic suction ( $\psi_o$ ). The sum of these two components is termed as total soil suction ( $\psi$ ). Please note that  $\psi_m$  and  $\psi_o$  is same as the soil-water potential discussed in the previous section. However,  $\psi$  is not same as total water potential since the former constitute only negative water potentials.  $\psi_m$  is due to the adsorptive and capillary force existing in the soil matrix where as  $\psi_o$  is the result of salts or contaminants present in the soil pore-water. In the absence of any contamination,  $\psi_m$  is equal to  $\psi$ . The common units for soil suction are kPa, Atm, pF, centibar. The unit pF is defined as the common logarithm of height in centimeters of the water column needed to provide the suction. Table 2.4 summarizes the relationship between different commonly used units of suction.

Table 2.4 Relationship between different units of soil suction

Height in cm of H <sub>2</sub> O column	pF (log cm of H <sub>2</sub> O column)	kg/cm <sup>2</sup>	kPa	Bar	Atmosphere (atm)
10	1	0.01	1	0.01	0.01
100	2	0.1	10	0.1	0.1
1000	3	1	100	1	1
10000	4	10	1000	10	10

WRCC obtained by drying and wetting the soil sample is termed as desaturation (desorption) and saturation (adsorption) curve, respectively. A typical drying and wetting WRCCs is presented in Fig. 2.12, which indicates a continuous 'S' shaped hysteretic relationship. Due to hysteresis, drying WRCC has higher

suction than wetting curve for particular water content. Following are some of the key points that are relevant for WRCC:

1. The volumetric water content at saturation,  $\theta_s$ , describes the water content at which the soil is completely saturated and typically depicts the initial state for the evaluation of the drying path.
2. The air-entry value (AEV),  $\psi_a$ , is the suction at which air enter the largest pore present in the soil sample during a drying process. AEV is less for coarse soil as compared to fine soils.
3. Residual water content ( $\theta_r$ ) is the minimum water content below which there is no appreciable change in  $\theta$ . Suction corresponding to  $\theta_r$  is called residual soil suction,  $\psi_r$ .
4. The water-entry value,  $\psi_w$ , on the wetting WRCC, is defined as the matric suction at which the water content of the soil starts to increase significantly during the wetting process.

A fully saturated soil specimen having a volumetric water content of  $\theta_s$  desaturates in three stages as depicted in Fig. 2.12. In stage 1 termed as capillary saturation zone extending up to AEV, the soil remains saturated with the pore-water held under tension due to capillary forces. In the desaturation zone (stage 2), ranging from AEV to  $\psi_r$ , there is a sharp decrease in water content and the pores are increasingly occupied by air. The slope of the WRCC in this portion describes the rate of water lost from the soil. In the third stage known as zone of residual saturation ( $>\psi_r$ ), there is little hydraulic flow. However, there may be some water vapour movement. Beyond this point, increase in soil suction does not result in significant changes in water content. The zone of residual saturation is terminated at oven dry conditions (i.e. water content equal zero), corresponding to a theoretical soil suction of approximately  $10^6$  kPa (Fredlund and Rahardjo 1993).



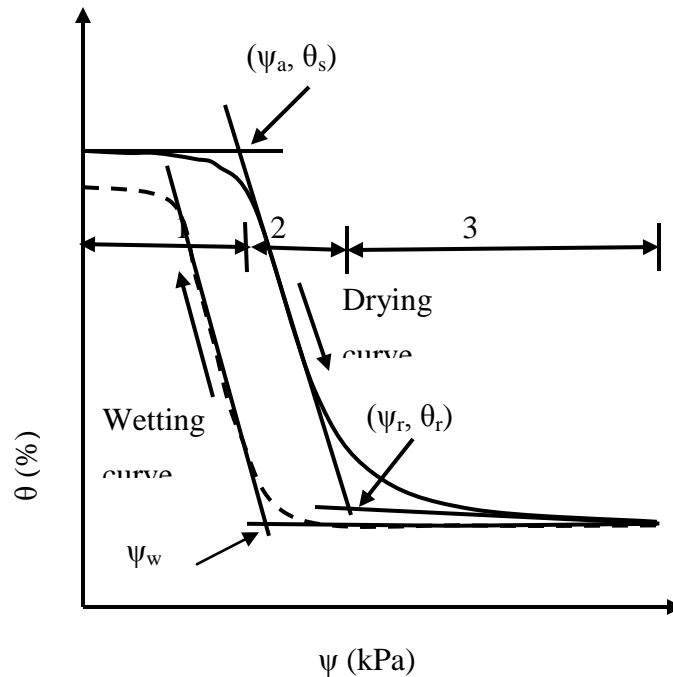


Fig. 2.12 Details of idealized WRCC

The slope of WRCC is termed as specific capacity or differential water capacity and represented by  $C(\theta) = (d\theta/d\psi)$ . This is an important property describing water storage and water availability to plants. As  $C(\theta)$  is more, water drained out or water availability from that soil is more. For a particular increase in  $\psi$ , the coarse grained soil releases more water than fine grained soil.

A large variety of instruments are available for measuring  $\psi_m$  or  $\psi$  in the field or in the laboratory, either directly or indirectly. A summary of various instruments used for measuring soil suction is presented in Table 2.5. Each of these measurement techniques has its own limitations and capabilities, and active research is ongoing for further improvement.

Table 2.5 Details of different suction measuring instruments

Method	Instrument	Suction	Usage	Range (kPa)	Equilibrium time
Direct	Tensiometer	M	F	0-80	Hours
	Pressure plate apparatus	M	L/F	0-5000	Hours
	Pressure membrane extractor	M	L/F	0-1500	Hours
	Ridley and Burland's apparatus (suction probe)	M	L	100-1000	Minutes
	NTU Mini suction probe	M	L	100-1500	Minutes
	Suction plate	M	L	0-90	Hours
	Gypsum block	M	F	60-600	Days
	Standpipe lysimeter	M	L	0-30	Days - Months
Indirect	Filter paper-contact	M	L/F	100-1000	2-5 Days
	Filter paper-non contact	T	L/F	1000-10000	2-14 Days
	Transistor psychrometer	T	L	100-10000	Hours
	Thermocouple psychrometer	T/ M	L	100-7500	Hours
	Thermal conductivity sensor	M	L/F	10-1500	Hours-Days
	TRL suction probe	T	F	1000-30000	Weeks
	Gypsum block	M	F	60-600	Days
	Centrifuge method	M	L	High	Depends on soil
	WP4 dewpoint potentiometer	T	L	0-40000	Minutes
	Pore fluid squeezer	O	L	Entire range	-
	Time domain reflectometry	M	L	Entire range	6-48 Hours
	Electrical conductivity sensor	M	L/B	50-1500	6-50 Hours
	Chilled-mirror psychrometer	T	L	500-300000	Minutes
	Vacuum dessicator	T	L	$10^3$ - $10^5$	Months
	Porous block	M	F	30-30000	Weeks
	Thermal block	M	F	0-175	Days
Equitensiometer	M	F	0-1000	Days	
Xeritron sensor	T	L	Entire range	Hours	

## WRCC models and estimation

It is noted that most of the instruments reported above have limited range of suction measurement. Therefore, several empirical or semi-empirical mathematical models have been developed for representing WRCC. The parameters of these models can be obtained by using the limited range of measured suction data. Once the parameters are known, the same can be used for extrapolating or interpolating the results by using the WRCC model. These WRCC parameters are important input for many of the mathematical models dealing with unsaturated soils. Two such models which are used widely in the literature are van Genuchten (1980) model and Fredlund and Xing (1994) model represented by Eqs. 2.35 and 2.36, respectively.

$$\theta(\psi) = \theta_r + (\theta_s - \theta_r) \left[ \left[ 1 + \left( \frac{\psi}{a_{vg}} \right)^{n_{vg}} \right]^{m_{vg}} \right]^{-1} \quad (2.35)$$

$$\theta(\psi) = \theta_s \left[ 1 - \frac{\ln \left[ 1 + \frac{\psi}{h_r} \right]}{\ln \left[ 1 + \frac{10^6}{h_r} \right]} \right] \left[ \left[ \ln \left[ \exp(1) + \left( \frac{\psi}{a_f} \right)^{n_f} \right] \right]^{m_f} \right]^{-1} \quad (2.36)$$

where  $\theta(\psi)$  is the volumetric water content at any suction,  $\psi$ ;  $\theta_r$  is the residual volumetric water content;  $\theta_s$  is the volumetric water content at saturation;  $a_{vg}$  and  $a_f$  are fitting parameters primarily dependent on the air entry value (AEV);  $n_{vg}$  and  $n_f$  are fitting parameters that are dependent on the rate of extraction of water from the soil;  $m_{vg}$  and  $m_f$  are fitting parameters which depend on  $\theta_r$ ;  $h_r$  is the suction (in kPa) corresponding to residual state. There are several such simplified and complex models reported in the literature for defining WRCC.

The experimental procedures adopted for determining SWCC are time consuming and cost-intensive. Therefore, attempts have been made by researchers to develop functions (such as pedo transfer functions) for the quick estimation of WRCC without performing extensive suction measurements. In

such cases, WRCC is based on soil physical parameters that can be quickly determined in the lab. This indirect approach is less time-consuming, simple, and more economical. However, such estimations can be soil-specific and case-specific and would depend mostly on the data used for developing the procedure. Therefore, estimated WRCC should be used with caution and only in those cases where suction measurements cannot be performed. For important projects it is always preferable to obtain measured WRCC for the soil. For more details on WRCC estimation, readers are requested to go through the wide range of literature available (Fredlund et al. 1998; Mbagwu and Mbah 1998; Fredlund et al. 2002; Matula et al. 2007; Nimmo et al. 2007; Soil vision 4.10)

### **Complexity in modelling the behaviour of unsaturated soil**

As discussed above, all the properties of unsaturated soil such as seepage, strength, and volume change behaviour are dependent upon the suction existing in the soil. These properties changes when the state of unsaturation changes and suction changes. The state of unsaturation is defined by  $\theta$ ,  $w$  or  $S_r$ . As against the steady state behaviour in saturated soil, an unsaturated soil therefore exhibit transient behaviour. The complex behavioural modelling of unsaturated soil is explained with respect to unsaturated hydraulic conductivity ( $k_u$ ) and flow as an example.

In the case of saturated soil, hydraulic conductivity ( $k_s$ ) remains constant with time. This is mainly due to the fact that all the pores are filled with water. In the case of unsaturated soil there is retention forces (suction) acting on water that would restrict easy movement. Due to this, hydraulic conductivity of unsaturated soil drastically reduces and is essentially a function of water content or suction present in the soil. For a particular soil,  $k_u$  increases as suction decreases till it approaches  $k_s$  as shown in Fig. 2.13 (Malaya 2011). This is mainly due to the fact that suction decreases due to the increase in water content which results in the increase in  $k_u$ . Therefore, it is clear that  $k_u$  is a function and changes with water content or suction. These functions are highly non-linear and laborious to determine experimentally. Mostly  $k_u$  functions are estimated

indirectly from water-retention characteristic curve (or SWCC), which is relatively easy to determine experimentally.

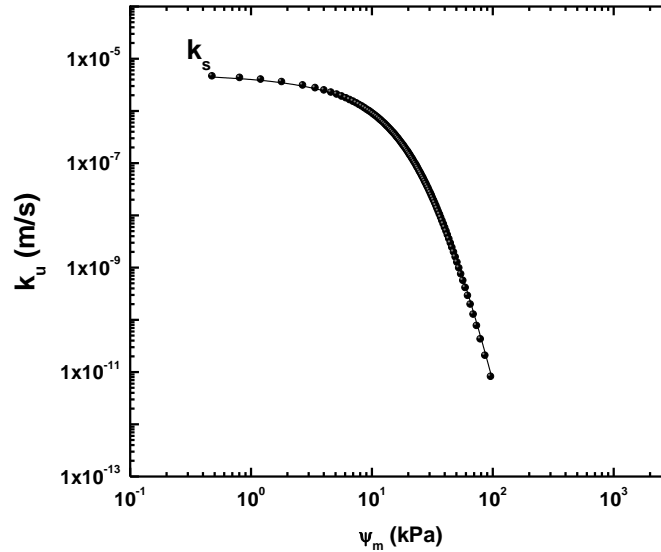


Fig. 2.13 Variation of unsaturated hydraulic conductivity with suction (Malaya 2011)

The 1-D flow through unsaturated soil can be represented by Darcy’s law expressed in the form of Eq. 2.37 where the flux density  $q$  is given by

$$q = k(h) \frac{\partial H}{\partial z} \quad (2.37)$$

where  $q$  is the flux density or Darcy velocity,  $H$  is the total soil water potential,  $z$  is the distance in the direction of flow,  $k(h)$  is the hydraulic conductivity which is a function of matric suction head.

$$H = z + h$$

$z$  is the gravitational head and  $h$  is the matric suction head or pressure head in general. In the case of unsaturated state of the soil, pressure head will be matric suction head or negative pressure head.

$\frac{\partial H}{\partial z}$  is the hydraulic gradient represented by “ $i$ ” which can also equal to

$$\frac{\Delta H}{\Delta z}$$

$$\text{Average } i = \frac{\Delta H}{\Delta z} = \frac{(h_{n+1} + z_{n+1}) - (h_n + z_n)}{(z_{n+1} - z_n)}$$

$n$  increases downwards and reference datum is ground surface.

$$\frac{\Delta H}{\Delta z} = \frac{\Delta h + \Delta z}{\Delta z} = 1 + \left( \frac{\Delta h}{\Delta z} \right)$$

**Problem:** For a soil, matric potential head is -75 cm and -50 cm at depth 150 cm and 200 cm, respectively. Given  $\theta = a |h|^{-b} |h| > 45$  cm and  $k = me^{n\theta}$ .  $a = 1000$ ,  $b = 2$ ,  $m = 10^{-12}$ ,  $n = 45$ ,  $k$  is in m/s. Determine soil water flux in m/s and flow direction. Distance downward is -ve and reference is ground surface.

$$\text{Average } i = 1 + \left( \frac{\Delta h}{\Delta z} \right)$$

$$= 1 + \left( \frac{-75 + 50}{-150 + 200} \right)$$

$$= 0.5$$

$$\theta = a (h)^{-b}$$

$$= 1000 \times |62.5|^{-2} \quad \text{h is the average value } (75+50)/2$$

$$= 0.256$$

$$k = 10^{-12} \times e^{(45 \times 0.256)}$$

$$= 1.007 \times 10^{-7} \text{ m/s}$$

$$\text{Flux } q = k \frac{\Delta H}{\Delta z}$$

$$= 1.007 \times 10^{-7} \times 0.5$$

$$= 5 \times 10^{-8} \text{ m/s}$$

Total potential: at 150 cm = -225 cm and at 200 cm = -250 cm. The flow will take place in the downward direction.

### Soil water diffusivity

While dealing with most of the flow problems in hydrology and geoenvironmental engineering, the term soil water diffusivity becomes important.

According to Darcy's law, flow density is defined by Eq. 2.37 which is re-written below:

$$q = -k(h) \frac{\partial H}{\partial z}$$

In the above,  $\frac{\partial H}{\partial z}$  can be re-written as  $\frac{\partial H}{\partial \theta} \times \frac{\partial \theta}{\partial z}$

$\frac{\partial H}{\partial \theta}$  is the inverse of specific water capacity (C) where in H is considered as the suction head.

Therefore the above equation becomes  $q = \frac{-k(h)}{C} \frac{\partial \theta}{\partial z}$

In the above representation,  $\frac{k(h)}{C}$  is known as soil-water diffusivity (D) and its unit is  $m^2/s$ .

$$q = -D \frac{\partial \theta}{\partial z} \quad (2.38)$$

Eq. 2.38 is identical to Fick's first law of solute diffusion. Analytical solutions are proposed by researchers for the above differential equation for simple boundary conditions. This equation is suitable for highly unsaturated state of the soil and is not valid of near saturated soil. For nearly saturated soil C approaches zero.

### **2.2.2 Different soil-water-contaminant interaction mechanisms**

The contaminants that can pose serious threat to humans persist in short or long interval of time. These contaminants can be naturally occurring ones such as arsenic, fluoride, traces of mercury or anthropogenic substances such as chlorinated organics, dissolved heavy metals etc. The major role of a geoenvironmental engineer is to predict the fate of contaminants in the subsurface and minimize its migration towards groundwater source. Fate prediction is very essential to understand the presence of contaminants in groundwater sources or subsurface for long term (50 to 200 years). This would essentially depend on different interaction mechanisms between contaminant and soil solids and also between contaminant and dissolved solutes present in

pore water. The knowledge is required to assess the risk or threat posed by these contaminants to humans and other organisms. Also, the performance and acceptable criteria of engineered barriers, which minimizes the risk of these contaminants is assessed based on fate predictions.

Fate of contaminant in geoenvironment is decided by retention and transport of contaminants. The important mechanisms governing these factors are as follows (Yong 2001):

**(A) Chemical mass transfer and attenuation**

- (a) Sorption- contaminant partitioning
- (b) Dissolution/ precipitation- addition or removal of contaminants
- (c) Acid-base reaction- proton transfer
- (d) Redox reaction- electron transfer
- (e) Hydrolysis/ substitution/ complexation/ speciation- ligand-cation complexes.

**(B) Mass transport**

- (a) Advection- fluid flow
- (b) Diffusion- molecular migration
- (c) Dispersion- mixing

**(C) Other factors**

- (a) Biological transformations
- (b) Radioactive decay

An adequate knowledge of these mechanisms is required to predict the fate of contaminant. When the contaminated pore fluid passes through the soil mass, it is bound to undergo weak or strong reactions. Sorption process in which the contaminants clings on to the soil solids is one of the predominant reactions. Such a reaction does not ensure permanent removal of contaminants from the pore fluid, rather attenuation takes place. Attenuation is the reduction in contaminant concentration during fluid transport due to retardation, retention and dilution. The extent of interaction between the contaminants and soil fraction determines reversible or irreversible nature of contaminant partitioning. The term retention is used for strong sorption of contaminants on the soil particles such that the concentration of pore fluid decreases with time. The amount of



contaminant concentration reaching a particular target is considerably less than the source concentration. Chemical mass transfer and irreversible sorption removes the contaminants from the moving pore fluid. This is a very important aspect for a contaminant barrier system, where in the contaminants reaching ground water is minimized. Retardation is mainly governed by reversible sorption and hence release of contaminant would eventually occur. This will ensure the delivery of the entire contaminant load to the final target (example ground water), but with much delay. The process of retention and retardation is depicted in Fig. 2.14. From the figure, it can be noted that for retention process, the area under the curves (concentration) goes on reducing. For retardation, the area remains constant (mass conservation), however the concentration of a particular contaminant reduces. In nature, the effect of contaminated pore fluid is reduced when it interacts with fresh water (especially during precipitation). This process of dilution also delays the contaminant migration. However, the process of dilution is mostly independent of soil interaction.

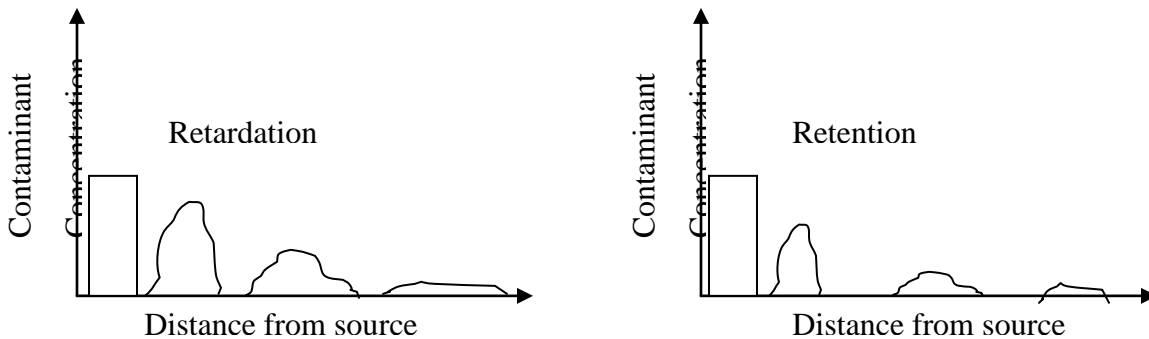


Fig. 2.14 Attenuation process due to soil-contaminant interaction

For an effective waste management, retention process is more ideal than retardation. For proper prediction of contaminant fate, it is very essential to know whether the contaminant is retained or retarded. The important reactions determining attenuation are discussed as follows:

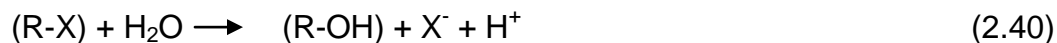
### 1) Hydrolysis

Hydrolysis is the reaction of  $H^+$  and  $OH^-$  ions of water with the solutes and elements present in the pore water. Such a reaction would continue only if the reaction products are removed from the system. Water is amphoteric in nature

(Yong 2001), which means it can act as acid or base. According to Bronsted-Lowry concept an acid is a proton donor and base is a proton acceptor. According to Lewis, acid is an electron acceptor and base is an electron donor. As discussed earlier, soil minerals have ionized cations and anions (metal ions) attached to it that results in a particular pH level in soil-water system. Hydrolysis reaction of metal ions can be represented as



The reaction increases with decrease in pH, redox potential and organic content and increases with temperature. Hydrolysis can be an important reaction in the process of biodegradation. For example,



where R is an organic molecule and X is halogen, carbon, nitrogen or phosphorus and is resistant to biodegradation. The reaction introduces OH in place of X making organic molecule susceptible to biodegradation.

## 2) Oxidation-reduction (redox) reaction

Oxidation-reduction (redox) reaction involves transfer of electrons between the reactants. In general, transfer of electrons is followed by the proton transfer also. Soil pore water provides medium for oxidation-reduction reaction which can be biotic and/or abiotic. Microorganisms present in the soil utilize oxidation-reduction (redox) reactions as a means to derive energy required for its growth. Hence, these microorganisms act as catalysts for reactions (redox) involving molecular oxygen, soil organic matter and organic chemicals. For inorganic solutes, redox reaction results in the decrease or increase in the oxidation state of the atom. This is important because some ions have multiple oxidation states and hence would influence the soil-contaminant interaction. It is found that biotic redox reactions are more significant than abiotic redox reaction.

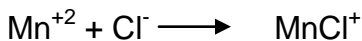
The redox potential Eh represented by Eq. 2.41 determines the possibility of oxidation-reduction reaction in the soil-contaminant system.

$$Eh = pE \left( \frac{2.3RT}{F} \right) \quad 2.41$$

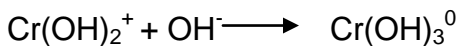
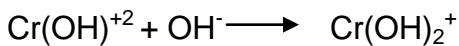
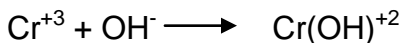
E is the electrode potential, pE represent negative logarithm of electron activity  $e^-$ , R is the gas constant, T is the absolute temperature, and F is the Faraday constant. At a temperature of 25<sup>0</sup>C,  $E_h = 0.0591pE$ . Factors affecting  $E_h$  include pH, oxygen content or activity, and soil water content.

### 3) Complexation

Complexation is the reaction between metallic cations and anions called ligands. The inorganic ligands such as  $Cl^-$ ,  $B^-$ ,  $F^-$ ,  $SO_4^{-2}$ ,  $PO_4^{-3}$ ,  $CO_3^{-2}$  and organic ligands such as amino acids take part in complexation reaction. For example,



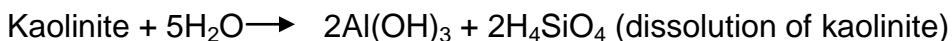
Complexation can also occur in series, such that complex formed from one reaction can react with another ligand as shown below (Reddi and Inyang 2000).



This indicates that the concentration of metals in the form of complexes also needs to be taken into account in addition to the free metal ion concentration. Else, the concentration of the metal transported downstream would always be more than the predicted concentration of metal ion.

### 4) Precipitation and dissolution

The process of precipitation and dissolution is an important mass transfer mechanism in the subsurface, where in dissolution increases and precipitation decreases the concentration of contaminants in pore water. Water is a good solvent for a variety of solids, liquids and gases. Dissolution is the process of complete solubility of an element in groundwater. Some natural minerals also undergo dissolution. For example,



Precipitation is reverse process of dissolution where in dissolved element comes out of the solution due to the reaction with dissolved species. Due to precipitation, the concentration of the element reduces in pore water. For

example, Lead gets precipitated from pore water due to its reaction with sulfides, carbonates or chlorides. Iron, zinc and copper precipitates due to hydrolysis reaction, and chromium, arsenic precipitates due to redox reaction. In some cases, both dissolution and precipitation occurs one after the other as the pore water advances.

pH is important factor governing dissolution and precipitation. An element has a solubility limit in water. Beyond the solubility limit the solution becomes supersaturated and starts precipitating. pH governs the solubility limit and hence when pH changes, there is a possibility of precipitation reaction. It is found that solubility reduces with pH, reaches a minimum value and then again increases. This indicates that there exists an optimal pH where precipitation will occur. Metal hydroxides are amphoteric (increasingly soluble at both low and high pH) and the pH for minimum solubility (optimum precipitation) is different for different metal. For example, cadmium-pH 11, copper-pH 8.1, chromium-pH 7.5, zinc-pH 10.1, nickel-pH 10.8. A small change in pH would therefore result in considerable changes in precipitation reaction.

## **5) Exsolution and volatilization**

This process involves mass transfer between gaseous and liquid or solid phase. Similar to precipitation this process removes mass from pore fluid to gaseous phase. This process is mostly governed by the vapour pressure (pressure of gaseous phase) with respect to liquid or solid at a particular temperature. There are a lot of volatile contaminants disposed into subsurface that finds its way to atmosphere. A thorough knowledge on the exsolution and volatilization is required to understand the mass transfer mechanism of these organic contaminants.

## **6) Radioactive decay**

In this process, unstable isotopes decay to form new ones with release of heat and particles from element nucleus. The process is known as  $\alpha$  or  $\beta$  decay depending on whether the element loses  $\alpha$  particle (helium) or a  $\beta$  particle (electron). The process of decay is irreversible and daughter isotope increases in

quantity. The disposal of radioactive waste generated from nuclear installations, mining etc. to subsurface will considerably increase the heat. Moreover, the radioactive isotope such as uranium, plutonium, cesium etc gets transported to far field and would pollute the groundwater. Preventing such harmful pollution and reducing the ill effect of overheating of subsurface is a challenging geoenvironmental problem.

### **7) Sorption and partitioning**

When contaminant laden pore water flow past the soil surface, mass transfer of these contaminants takes place on to the solids. The process is referred to as sorption or partitioning. The amount of partitioning depends on the soil surface (sorbent) and the reactivity of contaminant (sorbate). This is one of the predominant mechanisms governing the fate of contaminant once it is released into the geoenvironment. The term sorption refers to the adsorption of dissolved ions, molecules or compounds on to the soil surface. The mechanism of sorption includes physical and chemical sorption as well as precipitation reaction. These reactions are governed by surface properties of soil, chemistry of contaminant and pore water, redox potential and pH of the environment. Physical adsorption refers to the attraction of contaminant on to the soil surface mainly due to the surface charge (electrostatic force of attraction). Physical sorption is weak bonding and can be reversed easily by washing with extracting solution. Chemical sorption is strong force of attraction due to the formation of bonds such as covalent bond. High adsorption energy is associated with chemical sorption and it can be either exothermic or endothermic reaction. The details of sorption reaction and mass transport mechanisms will be discussed in detail in module 3 on how to use these information for predicting the fate of contaminants in geoenvironment.

### **8) Biological transformation**

Biological transformation is the degradation or assimilation of contaminants (mostly organic) by microorganisms present in the soil. Transformations from biotic processes occur under aerobic or anaerobic conditions. The transformation products obtained from each will be different. The

biotic transformation processes under aerobic conditions are oxidation reaction. The various processes include hydroxylation, epoxidation, and substitution of OH groups on molecules (Yong 2001). Anaerobic biotic transformation processes are mostly reduction reaction, which include hydrogenolysis,  $H^+$  substitution for  $Cl^-$  on molecules, and dihaloelimination (Yong 2001). The major application of biological transformation is in organic contaminant remediation which is discussed in module 4.

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## Model Questions

The knowledge of clay minerals is important in geoenvironmental engineering.

Explain?

Summarize important properties of clay minerals.

Bring out the major difference between the three clay minerals: Kaolinite, Illite and montmorillonite.

What are the important mechanisms of soil-water interaction?

Explain the formation of diffused double layer.

What are the important assumptions for formulation DDL theory?

Discuss in brief, Gouy Chapman DDL model.

Explain the significance of cation exchange capacity and method of its determination.

How does CEC and SSA influence reactivity of soil?

Define volumetric water content? How does the volumetric water content influence the flow properties of a soil medium?

Derive relationship between volumetric and gravimetric water content.

What are the different components of soil-water potential?

Compare saturated and unsaturated state of soil?

Explain important features of water retention curve?

Explain the complexity in modeling unsaturated behavior as compared to that of saturated soil.

Discuss soil-water diffusivity.

Explain in detail the various contaminant retention and transport mechanisms in soil.

What is the difference between retardation and retention of contaminants?

Discuss in detail, the important contaminant attenuation reaction in soil.

Explain the significance of soil sorption behavior in waste management?

Fig. Q2.1 represents the equilibrium condition (after time  $t$ ) of water separated from NaCl by using a semi-permeable membrane at a room temperature of  $27^{\circ}\text{C}$ .

There is a rise in solution level by 5 cm.

Illustrate using a figure, the condition at time  $t=0$  and explain what has happened thereafter till time  $t$  and why?

Calculate the molar concentration of the NaCl solution. The value of  $R$  is  $0.0820 \text{ Litre.atm/Kelvin.mole}$ . The density of NaCl is  $1.2 \text{ g/cc}$ . ( $1 \text{ atm}=0.1 \text{ MPa}$ ).

