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2
Basic Definitions and Concepts: Soil Components and Phases

Most soils consist of four components and three phases (Fig. 2.1). The four components include inorganic solids, organic solids, water, and air. Inorganic components are primary and secondary minerals derived from the parent material. Organic components are derived from plants and animals. The liquid component consists of a dilute aqueous solution of inorganic and organic compounds. The gaseous component includes soil air comprising a mixture of some major (e.g., nitrogen, oxygen) and trace gases (e.g., carbon dioxide, methane, nitrous oxide). Under optimal conditions for growth of upland plants, the solid components (inorganic and organic) constitute about 50% of the total volume, while liquid and gases comprise 25% each (Fig. 2.2a). Rice and other aquatic plants are exceptions to this generalization. The organic component for most mineral soils is about 5% or less. Immediately after rain or irrigation, the entire pore space or the voids in between the solids are completely filled with water, and the soil is saturated (Fig. 2.2b). When completely dry, the water in the pores is replaced by air or gases (Fig. 2.2c). General properties of components and phases are listed in Table 2.1. Under optimal conditions for some engineering functions, such as foundation for buildings and roads or runways, the pore space is deliberately minimized by compaction or compression. For such functions, the solid components may compose 80–90% of the total volume. There must be little if any liquid component for the foundation to be stable. Some industrial functions (e.g., dehalogenation) may require anaerobic conditions, however.

Anaerobiosis may lead to transformation of organic matter by the attendant methanogenesis and emissions of methane (CH_4) to the atmo-sphere. In contrast, oxidation and mineralization of organic matter may cause release of carbon dioxide (CO_2) to the atmosphere. Filtration of pollutants and sequestration of carbon (C) in soil as soil organic carbon (SOC), two important environmental functions, also depend on an optimal balance between four components and three phases. The dynamic equilibrium between components and phases can be altered by natural or anthropogenic perturbations.
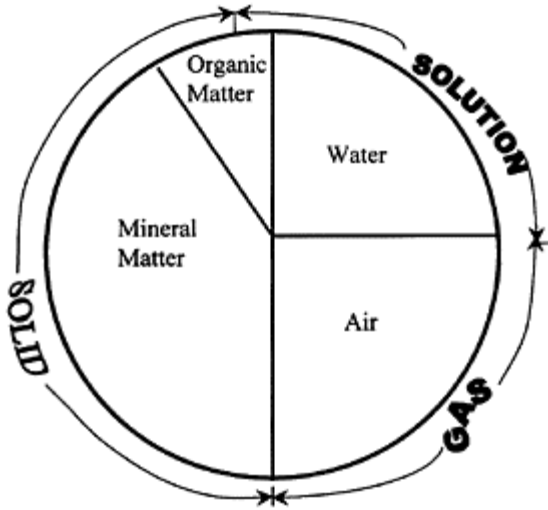
FIGURE 2.1 Soil is made up of four components and three phases.

2.1 DEFINITIONS

Soil physics deal with the study of soil physical properties (e.g., texture, structure, water retention, etc.) and processes (e.g., aeration, diffusion, etc.). It also consists of the study of soil components and phases, their interaction with one another and the environment, and their temporal and spatial variations in relation to natural and anthropogenic or management factors (Fig. 2.3). Soil physics involves the application of principles of physics to understand interrelationship of mass and energy status of components and phases as dynamic entities. All four components are always changing in their relative mass, volume, spatial and energy status due both to natural and management factors.
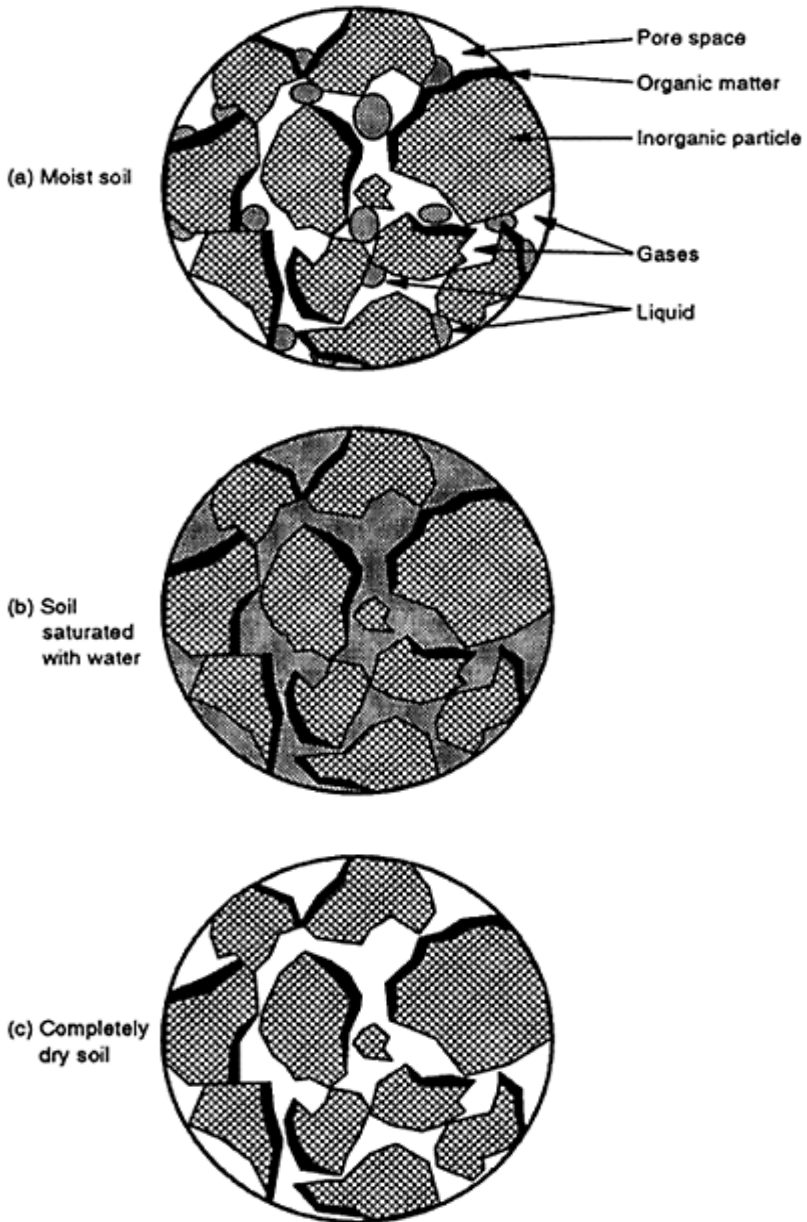
FIGURE 2.2 Interaction among four components and three phases for (a) moist, (b) water-saturated, and (c) completely dry soil.

Table 2.1 Properties and Phases and Components

Phases	Components	Composition	Properties
Solid	Inorganic	Products of weathering; quartz, feldspar, magnetite, garnet, hornblonde, silicates, secondary minerals	Skeleton, matrix ρ_s=2.0–2.8 Mg/m^3
	Organic	Remains of plants and animals; living organisms, usually <5%	Large surface area, very active, affects CO_2 in the atmosphere ρ_s=1.2− 1.5 Mg/m^3
Liquid	Soil solution	Aqueous solution of ions (e.g., Na, K, Ca, Mg, Cl, NO_3, PO_4, SO_4)	Heterogeneous, dynamic, discontinuous ρw=1.0 Mg/m^3
Gas	Soil air	N_2, O_2, CO_2, CH_4, C_2H_6, H_2S, N_2O, NO	ρ_a=1–1.5 kg/m^3 variable, dynamic

ρ_s=particle density, l_w=density of H2O, l_a=density of air.
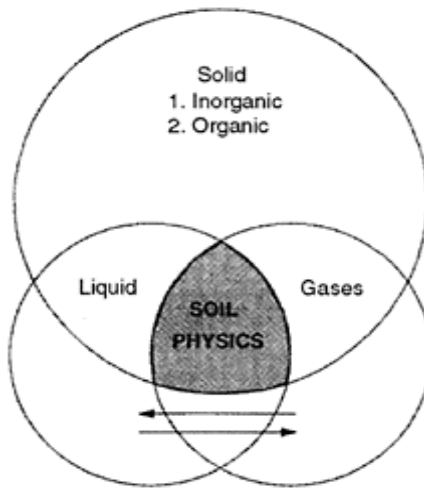

FIGURE 2.3 Soil physics is the study of properties and interaction among four components and three phases. Under optimal conditions for growth of upland plants, the solid phase composes about 50% of the total volume, and liquid and gaseous phases each compose 25% by volume. The volume of liquids increase at the expense of gases and vice versa.

Consider a unit quantity of soil with total mass (M_t) consisting of different components namely solids $(M_s$, which includes mass of inorganic component M_{in} and organic components $M_o)$, liquids (M_l) and gases $(M_g$, which is negligible and can be taken as zero for all practical purposes) (Fig. 2.4). Similarly, the total volume (V_t) comprises volume of its different components namely solids (V_s), which includes volume of inorganic components (V_{in}) and organic components (V_o), liquids (V_l) and gases (V_g). Different soil physical properties are defined in the following sections.
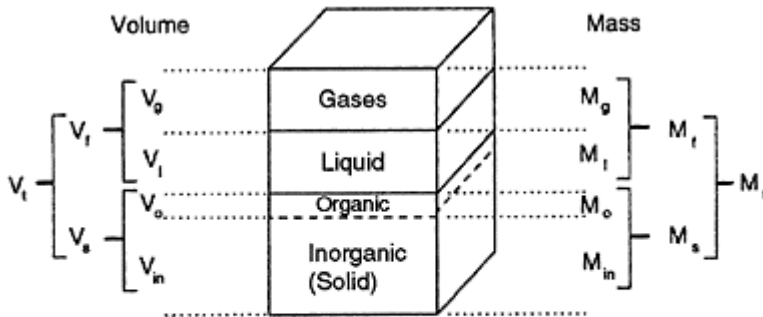
2.1.1 Soil Density (ρ)

Density is the ratio of mass and volume. It is commonly expressed in the units of g/cm^3 and Mg/m^3 (lbs/ft^3). Density is defined in four ways as follows:

1. *Particle density* (ρ_s): It is also called the true density, and is the ratio of mass of solid (M_s) divided by the volume of solid (V_s) [Eq. (2.1)].

$$\rho_s = M_s/V_s = (M_{in} + M_o)/(V_{in} + V_o)$$

(2.1)

$$V_t = V_g + V_l + (V_o + V_{in}) = V_g + V_l + V_s$$

$$M_t = M_g + M_l + (M_o + M_{in}) = M_g + M_l + M_s \cong M_l + M_s$$

FIGURE 2.4 A schematic showing the mass *(M)* and volume *(V)* relationship of four soil components. Subscripts *f, g, l, o, in, s,* and *t* refer to fluids, gases, liquid, organic, inorganic, solid, and total, respectively.

Particle density of inorganic soils ranges from 2.6 to 2.8 g/cm^3 or Mg/m^3, and those of minerals commonly found in soils is shown in Table 2.2. Note that density of organic matter is about half of that of the inorganic mineral. In comparison, the density of water is about 1.0 Mg/m^3 and that of the air about 1.0 kg/m^3.

2. *Bulk density (ρ_b):* It is also called the apparent density, and is the ratio of mass of solid *(M_s)* to the total volume *(V_t)*. Soil bulk density can be defined as wet *(ρ'_b)* that includes the mass of water [Eq. (2.2)], and dry *(ρ_b)* which is without water [Eq. (2.3)]. Its units are also that of mass/volume as g/cm^3 or Mg/m^3.

$$\rho'_b = \frac{M_s + M_w}{V_t} = \frac{(M_{in} + M_o + M_w)}{(V_s + V_w + V_g)} \tag{2.2}$$

$$\rho_b = \frac{M_s}{V_t} = \frac{M_{in} + M_o}{V_s + V_g} \tag{2.3}$$

In a dry soil, V_w is zero. Wet soil bulk density is an ever changing entity because of soil evaporation at all times under natural conditions. Therefore, soil bulk density is preferably reported as a dry soil bulk density. A dense soil has more solids per unit volume (Fig. 2.4a) than a porous soil (Fig. 2.5b). Methods of measurement of ρ_b are described by Campbell et al. (2000) and Culley (1993).

Table 2.2 Particle Density of Some Common Soil
Minerals, Organic Matter, Water and Air

Mineral	Particle density (Mg/m^3)	Other constituents	Particle density (Mg/m^3)
Biotite	2.7–3.3	Soil organic matter	1.0–1.4
Brucite	2.38–3.40	Water	1.0
Calcite	2.72–2.94	Air	10×10^{-3}
Chlorite	2.60–3.3		
Diamond	3.50–3.53		
Dolomite	2.86		
Gibbsite	2.38–2.42		
Geothite	3.3–4.3		
Gypsum	2.3–2.47		
Hematite	5.26		
Hornblende	3.02–3.45		
Illite	2.60–2.90		
Kaolinite	2.61–2.68		
Magnetite	5.175		
Montmorillonite	2.0–3.0		
Muscovite	2.77–2.88		
Orthoclase	2.55–2.63		
Pyrite	5.018		

Quartz	2.65
Serpentine	2.55
Talc	2.58–2.83
Tourmaline	3.03–3.25
Vermiculite	2.3

Source: Adapted from Handbook of Chemistry and Physics (1988).

3. *Relative density or specific gravity (G_s):* Specific gravity is the ratio of particle density of a soil to that of the water. Being a ratio, it is a dimensionless entity, and is expressed as shown in Eq. (2.4).

$$G_s = \rho_s/\rho w$$

(2.4)

4. *Dry specific volume (V_b):* It is defined as the reciprocal of the dry bulk density [Eq. (2.5)] and has units of volume divided by mass or cm^3/g or m^3/Mg.

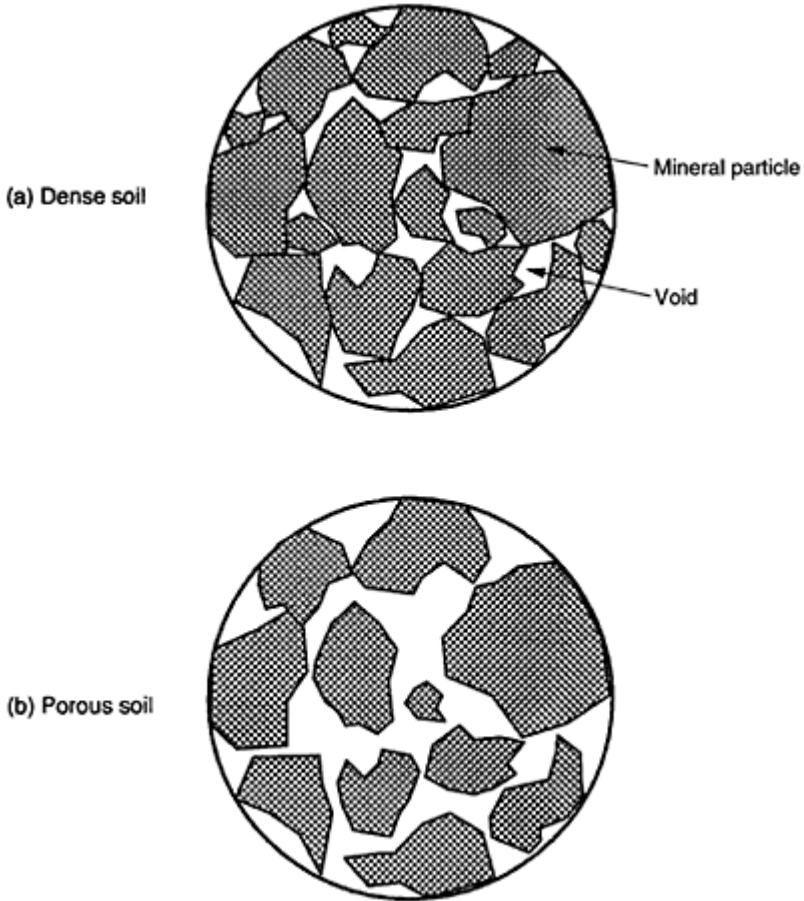$$V_b = \frac{1}{\rho_b} = \rho_b^{-1} = \frac{V_t}{M_s} = \frac{(V_s + V_f)}{(M_s + M_e)}$$

(2.5)

(a) Dense soil

Mineral particle

Void

(b) Porous soil

FIGURE 2.5 Dense soils are suitable
for engineering functions and porous
soils for agricultural land use.

2.1.2 Soil Porosity (*f*)

Porosity refers to the relative volume of voids or pores, and is therefore expressed as a fraction or percent of the total volume or of the volume of solids. Soil porosity can be expressed in the following four ways:

1. *Total porosity (f_t)*: It is the ratio of volume of fluids or water plus air *(V_f)* to total volume *(V_t)*, as shown in Eq. (2.6).

$$f_t = \frac{V_f}{V_t} = \frac{V_g + V_l}{V_s + V_l + V_g} \tag{2.6}$$

2. *Air-filled porosity (f_a):* It refers to the relative proportion of air-filled pores [Eq. (2.7)].

$$f_a = \frac{V_g}{V_t} \tag{2.7}$$

In relation to plant growth, the critical limit of air-filled porosity is 0.10 or 10%, below which plant growth is adversely affected due to lack of sufficient quantity of air or anaerobiosis. Air porosity is also equal to total porosity minus the volumetric moisture content (Θ) as computed in Eq. (2.11).

3. *Void ratio (e):* In relation to engineering functions, where porosity should be usually as low as possible, the relative proportion of voids to that of solids is expressed as void ratio [Eq. (2.8)]. Being a ratio, it is also a dimensionless quantity.

$$e = \frac{V_f}{V_s} = \frac{(V_g + V_l)}{(V_{in} + V_o)} \tag{2.8}$$

4. *Air ratio (α):* It is defined as the ratio of volume of air to that of the solids [Eq. (2.9)] and has relevance to plant growth and engineering applications.

$$\alpha = \frac{V_g}{V_s} = \frac{V_g}{(V_{in} + V_o)} \tag{2.9}$$

2.1.3 Soil Moisture Content

Soil moisture is the term used to denote water contained in the soil. Soil water is usually not free water, and is, therefore, called soil moisture. Soil moisture content can be expressed in the following four ways:

1. *Gravimetric soil moisture content (w):* It is the ratio of mass of water (M_w) to that of solids (M_s), and is expressed either as fraction or percent [Eq. (2.10)].

$$w = \frac{M_w}{M_s} = \frac{M_w}{(M_{in} + M_o)} \tag{2.10}$$

2. *Volumetric soil moisture content* (Θ): In relation to agricultural and engineering functions, it is more relevant to express soil moisture content on volumetric than on gravimetric basis. Similar to *w*, Θ is also expressed as a ratio or percent [Eq. (2.11)].

$$\theta = \frac{V_w}{V_t} = \frac{V_l}{(V_s + V_f)} \tag{2.11}$$

3. *Liquid ratio (θρ):* Just as in case of void ratio, the liquid ratio has also numerous engineering applications, and is expressed as a ratio [Eq. (2.12)].

$$\theta_\rho = \frac{V_w}{V_s} = \frac{V_w}{(V_{in} + V_o)} \tag{2.12}$$

The liquid ratio is also a useful property for soils with high swell-shrink properties.

4. *Degree of saturation (s):* It refers to the relative volume of pore space containing water or liquid in relation to the total porosity [Eq. (2.13)], and is also expressed as a fraction or percentage.

$$s = \frac{V_w}{V_f} = \frac{V_w}{(V_l + V_s)} \qquad\qquad 2.13$$

2.1.4 Soil Physical Quality

Thirteen soil physical properties defined above are extremely important in defining soil physical quality in relation to specific soil functions (see Chapter 1; Arshad et al., 1996; Lowery et al., 1996). The objectives of soil management are to optimize these properties for specific soil functions. One or an appropriate combination of these properties is used as an index of soil physical quality. Indicators of soil quality, however, differ among soils and specific functions. The normal range of these indicators is shown in Table 2.3.

General physical properties of three phases and four components are shown in Table 2.4. Solids form the skeleton of the soil or soil matrix in which fluids constitute the plasma. Particle density of the inorganic components is almost twice that of the organic components. The liquid phase is a dilute aqueous solution of numerous salts including nitrates, chlorides, sulphates, carbonates, and phosphate of K, Ca, Mg, Na, and other cations. Soil air or the gaseous phase contains more CO_2 and less O_2 than atmospheric air (see Chapter 18).

TABLE 2.3 Normal Range of Soil Physical Properties in Relation to Plant Growth

Soil physical property	Range	Units
Particle density (ρ_s)	2.6–2.8	g/cm^3, Mg/m^3
Dry bulk density (ρ_b)	0.7–1.8	g/cm^3, Mg/m^3
Porosity (f_t)	0.3–0.7	Fraction, m^3/m^3
Air porosity (f_a)	0–f_t	Fraction, m^3/m^3
Void ratio (e)	0.4–2.2	Fraction
Gravimetric soil moisture content (w)	0–0.3	Fraction, kg/kg
Volumetric soil moisture content (Θ)	0–0.7	Fraction, m^3/m^3
Degree of saturation (s)	0–1	Fraction
Dry specific volume (V_b)	0.5–1	cm^3/g, m^3/Mg
Air ratio (α)	0–1	Dimensionless
Liquid ratio (θ_ρ)	0–1	Dimensionless
Wet bulk density (ρ'_b)	1–2	g/cm^3, Mg/m^3

2.2 INTERRELATIONSHIP AMONG SOIL PROPERTIES

Several of these properties are interrelated and one can be computed from another. Specific examples of these interrelationships are shown below:

$\theta = w\rho_b/\rho_w$

$$(2.14)$$

$$\theta = \frac{\rho'_b - \rho_b}{\rho_w} \qquad (2.15)$$

$ft = (1 - \rho_b/\rho_s)$

$$(2.16)$$

$e = (\rho_s/\rho_b) - 1$

$$(2.17)$$

$\theta_{\rho} = \Theta(1+e)$

$$(2.18)$$

$f_t = f_a + \theta$

$$(2.19)$$

$\rho_b = \rho_s(1 - f_t)$

$$(2.20)$$

$$w = \frac{\rho'_b - \rho_b}{\rho_b} \qquad (2.21)$$

TABLE 2.4 General Properties of Phases and Components

Phase	Component	Composition	General properties
Solid	Inorganic	Products of weathering of rocks and minerals. Mostly comprise primary and secondary minerals e.g. quartz, feldspar, magnetite, garnet, hornblende, silicates, and secondary minerals. Usually compose 95% of the dry soil mass.	Skeleton, matrix, ρ_s of $2.6-2.8$ g/cm^3. Surface area and charge density depend on size distribution,
	Organic	Remains of plants and animals at various stages of decay and decomposition. Usually comprise <5% of the dry soil mass.	This fraction is highly reactive and dynamic. It has large surface area and high charge density. ρ_s ranges from 1.2 to 1.5 g/cm3.
Liquid	Soil solution	Aqueous and dilute solution of numerous ions. Predominant ions depend on the parent material and land use and may comprise Na, K, Ca, Mg, Cl, NO_3, PO_4, and SO_4.	This is a very heterogenous solution, and is highly variable in time and space. This phase is discontinuous and increases or decreases depending on the degree of wetness and density of soil.

| Gas | Soil air | Composition of soil air differs than that of the atmosphere. Soil air comprises a mixture of numerous gases including N_2, O_2, CO_2, CH_4, C_2H_6, H_2S, N_2O, NO, and others. | Composition of soil air is extremely heterogenous, very dynamic, and highly variable over time and space. This is also a discontinuous phase and varies inversely with volume of soil solution. Approximate density of soil air is 1–1.5 kg/m^3. |

2.3 ASSESSMENT OF SOIL PARTICLE DENSITY

Methods of assessment of ρ_b, f_t, f_a, w, and Θ are discussed under appropriate sections. There are two common procedures of determining soil particle density. One is based on calculations from the particle density of its constituents [Eq. (2.22)].

$$\frac{1}{\rho_s} = \frac{x_1}{\rho_{s1}} + \frac{x_2}{\rho_{s2}} + \frac{x_3}{\rho_{s3}}$$

(2.22)

where x_1, x_2, and x_3 are weight fractions of the constituents, and ρ_{s1}, ρ_{s2}, and ρ_{s3} are the corresponding particle densities of those fractions. The second method of determining the particle density involves the laboratory procedure based on the Archimedes' principle. This procedure involves measurement of the volume displacement of dry soil by a liquid of known density using a pycnometer (Blake and Hartge, 1986). In addition, eletronic pycnometers are also available.

Example 2.1

A soil is sampled by a core measuring 7.6 cm in diameter and 7.6 cm deep. The core weighs 300 g. The total core plus wet soil weight is 1000 g. On oven drying at 105° C the core plus dry soil weighed 860 g. Calculate wet and dry bulk densities and gravimetric moisture contents.

Solution
Total volume of core $= \pi r^2 h = 3.14 (3.8\ cm^2) \cdot 7.6\ cm = 345\ cm^3$
Core weight $= 300$ g
Weight of wet soil $= 1000$ g-300 g$=700$ g
Weight of dry soil $= 860$ g-300 g$=560$ g
Wet bulk density $(M_t/V_t) = 700$ g$/345\ cm^3 = 2.03\ g/cm^3$
Dry bulk density $(M_s/V_t) = 560$ g$/345\ cm^3 = 1.62\ g/cm^3$
Gravimetric moisture content $(w) = M_w/M_s = (1000$ g-860 g$)/ 560$ g
$= 140$ g$/560$ g
$= 0.25$ or 25%

Example 2.2

One liter of dry soil sampled from a farm requires 300 g of water to completely saturate it. Calculate: (a) its porosity and (b) volume of water required to saturate the plow layer (20 cm) of 1 hectare of the farmland.

Solution
(a) Porosity (ft)=V_w/V_f=300 cm³/1000 cm³=0.3 m³/m³
    (b) Depth of water $(Q)=f_t \cdot d$, where d is depth =0.3×20 cm=6 cm
    Total volume of water for one ha=6×10⁵ L

Example 2.3

A soil in the greenhouse container has a wet bulk density of 1.7 Mg/m³ and dry bulk density of 1.4 Mg/m³. Calculate gravimetric and volumetric soil moisture contents, and air-filled porosity.

Solution

$$w = \frac{\rho'_b - \rho_b}{\rho_b} = \frac{1.7 - 1.4}{1.4} = 0.214 \, \text{kg/kg}$$

$$\Theta = \frac{\rho'_b - \rho_b}{\rho_w} = \frac{1.7 - 1.4}{1.0} = 0.3 \, \text{m}^3/\text{m}^3$$

$$f_a = 1 - (V_s + V_w) = 1 - \left(\frac{1.4}{2.65} + 0.3\right) = 0.172 \, \text{m}^3/\text{m}^3$$

An alternative solution is to assume the volume of the container.
Let the pot volume=1000 cm3
Particle density=2.65 g/cm³
Wet soil weight=1000 cm³×1.7 g/cm³=1700 g
Similarly, dry soil weight=1400 g
Mass of water (M_w)=1700 g−1400 g=300 g
Volume of water (V_w)=300 cm³
Gravimetric moisture content (W)=300 g/1400 g=0.214 kg/kg or 21.4%
Volumetric moisture content (Θ)=300 cm³/1000 cm³=0.30 m³/m³ or 30%
Volume of solids=mass/density=1400 g/2.63 g/cm³=528.3 cm³
Air porosity (f_a)=(1000 cm³−528.3 cm³−300 cm³)/1000 cm³
=171.7 cm³/1000 cm³=0.172 m³/m³ or 17.2%

Example 2.4

One liter of soil has a wet weight of 1500 g, dry weight of 1200 g, and volume of soil solids of 450 cm^3. Compute all 13 soil physical properties.

Solution
1. $\rho_s = M_s/V_s = 1200 \text{ g}/450 \text{ cm}^3 = 2.67 \text{ g/cm}^3$
2. $\rho_b = M_s/V_t = 1200 \text{ g}/1000 \text{ cm}^3 = 1.20 \text{ g/cm}^3$
3. $\rho_b = (M_s + M_w)/V_t = 1500 \text{ g}/1000 \text{ cm}^3 = 1.5 \text{ g/cm}^3$
4. $G_s = \rho_s/\rho_w = 2.67$
5. $V_b = 1/\rho_b = 0.83 \text{ cm}^3/\text{g}$
6. $f_t = (1 - \rho_b/\rho_s) = (1 - 1.2/2.67) = 0.55 \text{ or } 55\%$
7. $f_a = 1 - (V_s + V_w) = 1 - (450/1000 + 300/1000) = 1 - 0.75 = 0.25 \text{ or } 25\%$
8. $e = Vf/V_s = 550 \text{cm}^3/450 \text{ cm}^3 = 1.22$
9. $\alpha = V_g/V_s = 250 \text{ cm}^3/450 \text{ cm}^3 = 0.56$
10. $w = 300 \text{ g}/1200 \text{ g} = 0.25 \text{ or } 25\%$
11. $\Theta = 300 \text{ cm}^3/1000 \text{ cm}^3 = 0.30 = (w.\rho_b/\rho_w)$
12. $\Theta_\rho = V_w/V_s = 300 \text{ cm}^3/450 \text{ cm}^3 = 0.67$
13. $s = V_w/V_f = 300 \text{ cm}^3/550 \text{ cm}^3 = 0.55$

Example 2.5

Calculate ρ_s of a mixture containing 48% by weight of quartz, 50% of vermiculite, and 2% by weight of soil organic matter.

Solution

From Table 2.1, ρ_s is 2.65 Mg/m^3 for quartz, 2.3 Mg/m^3 for vermiculite, and 1.4 Mg/m^3 for soil organic matter. The ρ_s is computed by substituting these values in [Eq. (2.22)]:

$$\frac{1}{\rho_s} = \frac{0.48}{2.65} + \frac{0.50}{2.3} + \frac{0.02}{1.4} = 0.181 + 0.217 + 0.014 = 0.412 \frac{\text{cm}^3}{\text{g}}$$

$$\therefore \rho_s = \frac{1}{0.412} \frac{\text{g}}{\text{cm}^3} = 2.43 \text{ g/cm}^3 \text{ or Mg/m}^3$$

PROBLEMS

1. Calculate particle density of a soil from the following data:
Weight of pycnometer=50 g
Weight of the powder dry soil=214 g
Mass of soil and deaerated water when pycnometer was filled to capacity + pycnometer=352 g
Temperature of water=20°C
Volume of pycnometer=168 cm^3

2. Consider the following data based on field measurements:
i. Diameter of the cylindrical core=5.05 cm
ii. Height of the cylindrical core=5 cm
iii. Weight of the core=150 g
iv. Weight of field soil+core=312.5 g
v. Weight of the oven dried (105°C) soil+core=282.5 g
vi. Weight of the oven dried (900°C) soil+core=276.0
Using the particle density calculated in Question 1, calculate W, Θ, ρ'_b, ρ_b organic fraction, and V_s.

3. Prove or disprove the following:
i. $f = \frac{e}{1+e}L / = We$
ii. $f=e+1$
iii. $e = \frac{f}{1-f}$
iv. $e=f-1$
v. $\Theta=sf$
vi. $\rho_b=V_s\rho_s+V_w\rho_w+V_a\rho_a$
vii. $V_w/V_s=\Theta(1+e)$
viii. $V_s\rho_s=\rho_b(V_s+V_w+V_a)$

4. A soil of one m³ total volume (V_t) has the following properties:
Vs=0.5
Vw=0.3
Va=0.2
Assuming $\rho_s=2.65$g/cm³, calculate:
(a) f, f_a, s, e, M_s and ρ_b
(b) What are the weight and volume of water required to saturate it?

5. In a greenhouse study, a soil is packed in a container at a ρ_b of 1.5 Mg/m³. The antecedent Θ is 0.2. Assuming the volume of the container is 1000 cm3, what is the volume of water needed to double the Θ of the entire soil?

6. A sample of moist soil weighed 100 g and had an oven dry moisture content (w) of 0.04. What is the oven dry weight (M_s) of the 100 g sample?

7. 10 mm of rain infiltrated a soil having an initial moisture content by volume (Θ) of 0.1 m3/m3. If the soil absorbed enough of the rainfall to raise its moisture content to 0.2 m³/m³, how many cm would the rainfall penetrate?

8. What are principal soil functions? Briefly describe each function.

9. How does application of soil physics improve environment quality?

10. Describe the term "sustainable use of soil and water resources."

11. How do soil constituents influence environment quality?

12. How do soil constituents influence agricultural sustainability?

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3
Soil Solids

Soil solids, comprising inorganic and organic components, form the matrix or the body of most soils. This matrix, or the visible part of the soil, is the storehouse of water and nutrient elements (e.g., N, P, K, Ca, Mg, Zn, Cu, etc.). It is also the site of most processes that govern soils buffering and filtering capacity, and life support capability. The buffering capacity of the soil refers to its ability to withstand or to adapt to sudden perturbations such as in soil reaction (i.e., pH). The filtering capacity refers to soil's ability to remove pollutants (e.g., pathogens or chemicals including heavy metals) out of the water percolating through the soil by denaturing pollutants or mechanical sieving of suspended particles. Both buffering and filtering capacities depend on soil's reactivity. The latter refers to chemical, physical, and biological reactions in soil and depends on its nature (e.g., relative proportion of the inorganic and organic components, coarse or fine size, small or large surface area, and low or high charge density). Soil quality is determined by these and other properties of soil solids, which in turn moderate the soil's ability to support plant and animal life. Soil's life support capability depends on processes that govern productivity, elemental cycling, and environment quality (see Chapter 1).

3.1 INORGANIC COMPONENTS

The inorganic components comprise more than 95% by weight of total solid fraction for most mineral soils. It is the product of weathering of parent material, and comprises a range of primary and secondary minerals. Important properties of the inorganic components are: (i) size, (ii) shape, (iii) surface area, (iv) clay minerals and charge properties, (v) swelling and shrinkage, (vi) water absorption and heat of wetting, and (vii) packing arrangement.

3.1.1 Particle Size Distribution or Soil Texture

The inorganic component comprises two types of soil particles, primary and secondary. Primary particles are discrete units that cannot be further subdivided, and are also called "soil separates." Secondary particles consist of primary particles and can be subdivided into its "separates" by chemical or mechanical dispersion. Particle size is an important

soil physical property. It affects total porosity, pore size, and surface area. Particle size distribution refers to the "quantitative" measure of the particle size that constitutes the solid fraction. In contrast, soil texture refers to a "qualitative" measure of particle sizes based on "feel" of the soil material, which may be coarse, gritty, fine, or smooth.

Size Fractions

Depending on the size distribution, primary particles (textural fractions) or soil separates are usually divided into three classes, e.g., sand, silt, and clay. There are numerous systems of classifying separates into different size classes. Most commonly used systems include: (i) the U.S. Department of Agriculture (USDA), (ii) the International Society of Soil Science (ISSS), (iii) the American Society of Testing Material (ASTM), (iv) the Massachusetts Institute of Technology (MIT), (v) the U.S. Public Road Administration (USPRA), (vi) the British Standard Institute (BSI), and (vii) the German Standards (DIN). There are other local and regional systems as well. The two most commonly used systems by soil scientists and agronomists are the USDA and the ISSS/IUSS (Table 3.1). The ASTM system is widely used by engineers.

Material >2mm is considered the nonsoil fraction in both USDA and ISSS/IUSS systems. Three principal textural classes of <2 mm components or the soil fraction are (i) sand, (ii) silt, and (iii) clay. General physical properties of these three fractions are listed in Table 3.2, and are briefly described below.

Sand. This is the coarse fraction, and constitutes the skeleton of the soil body. The sand fraction can be subdivided into coarse, medium,

TABLE 3.1 Two Widely Used Systems of Particle Size Distribution

The USDA System[a]		The ISSS System[b]	
Soil separate	Size range (mm)	Soil separate	Size range (mm)
Very coarse sand	2.00–1.00	coarse sand	2.00–0.20
Coarse sand	1.00–0.50	fine sand	0.20–0.02
Medium sand	0.50–0.25	silt	0.02–0.002
Fine sand	0.25–0.10	clay	<0.002
Very fine sand	0.10–0.05		
Silt	0.05–0.002		
Clay	<0.002		

Note: For both system particles of diameter (D)>2 mm are considered nonsoil (skeletal) fraction.
[a]$D=(ar)^{n-1}$, where $a=2$, and $r=1/2$.
[b]$D=ar^{n-1}$, where $a=2$, and $r=1/10$.

and fine fractions (USDA system) (Table 3.1). Sand grains comprise mostly quartz but also contain fragments of feldspar and mica, and traces of heavy minerals, e.g., zircon,

tourmaline, and hornblende. Sand particles are jagged, hard (hardness of 5 to 7 on mhos scale) (Table 3.2), and can abrade steel as is evident by wearing down of the plow.

Silt. This is an intermediate size fraction, and also constitutes the skeleton of the soil. Properties of coarse silt fraction are similar to that of sand, but that of the fine silt approach that of clay. Mineralogical composition of silt is similar to that of sand, but silt has more surface area (see Section 3.3 in this chapter). Primary minerals present in sand and silt fractions are listed in Table 3.3.

Clay. This is the fine fraction, and constitutes the reactive fraction of the soil. Because of its very fine size, the clay fraction is colloidal, highly reactive, has large surface area, and high charge density. In shape, the clay particles are plate-like or needle-like. In mineralogy, the clay particles comprise a group of clay minerals, called *alumino-silicates*. These are secondary clay minerals, and also contain fine particles of iron oxide (Fe_2O_3), aluminum oxide (Al_2O_3), calcium carbonate ($CaCO_3$), and other salts. Because of its larger surface area, the clay fraction has the most influence on many soil properties. Properties of the clay fraction with a notable influence on soil behavior are listed in Table 3.2 and include: (i) easy hydration because of its high affinity for water, (ii) high swell/shrink capacity because of the expanding nature of the clay lattice, (iii) high

TABLE 3.2 Some Physical Properties of Soil Separates

Property	Soil separates		
	Sand	Silt	Clay
Size	2–0.02 mm	0.02 mm–0.002 mm	<0.002 mm
Shape	Jagged	Slightly irregular	Platy/tube-like
Feel	Gritty	Smooth, floury	Sticky
Plasticity	Not plastic	Slightly plastic	Plastic
Cohesion	Not cohesive	Slightly cohesive	Cohesive, gelatinous
Surface area	Very low	Moderate	Very high
Mineralogy	Primary	Primary minerals	Secondary clay minerals
Heat of wetting	None	Minimal	High
Secondary particles	None	Few	Forms aggregates
Water holding capacity	None/slight	Moderate	High, hygroscopic
Hardness	5.5–7 (on the mhos scale)	5.5–7.0	—
Ion exchange capacity	None	Very low	High to very high

TABLE 3.3 Common Primary Minerals Found in
Sand and Silt Fractions

Mineral	Weatherability
Quartz	Most resistant
Muscovite	↓
Microline	
Orthoclase	↓
Biotite	
Albite	↓
Horneblende	
Augite	↓
Anorthite	
Olivine	Least resistant

Source: Adapted from Brady and Weil 2002.

plasticity because of its ability to retain shape when a moist clay is molded, (iv) sticky when moist and crack because of shrinking, and cake when dry because of the cohesive forces, and (v) high density of negative charge leading to formation of electrostatic double layer when fully hydrated because of the deficit created by ionic substitution or broken bonds/edges. Some of these properties are discussed in detail in this and the following chapters.

Assessment of Particle Size Fractions

The process of determination of particle size distribution is called mechanical analysis. The procedure has two-steps: dispersion and fractionation. Dispersion involves removal of cementing material (compounds or substances which bind the particles together) to break secondary particles into primary particles or soil separates. Dispersion agents used in this determination depend on the nature of the cementing material (Table 3.4). For example, hydrogen peroxide (H_2O_2) is used to remove organic material, dilute acid to remove carbonates/electrolytes, and sodium dithionite to remove sesquioxides. The latter are compounds in which the ratio of metal to oxygen is 2:3 (M_2O_3 where M is a metalic ion such as Fe, Al, Mn, etc.).

Fractionation is the process of physically separating the particles into different size ranges. A wide range of methods of fractionation are used (Table 3.5), and the choice of an appropriate method depends on the particle size, objectives, and the facilities available. Two of the most commonly used procedures in soil physics laboratory are sieving

TABLE 3.4 Dispersive Agents Needed to Remove
Binding Agents Prior to Mechanical Analysis

| Cementing material	Dispersion agent
Organic matter	Hydrogen peroxide (H_2O_2)
Oxides of Fe and Al	Treatment with oxalic acid, sodium sulfide, sodium dithionite, and sodium citrate
Electrolytes	Dissolution and leaching with dilute acids, electrodialysis, and sodium hexametaphosphate
Cohesion/adhesion	Rehydration by boiling in H_2O, shaking, trituration, stirring, and ultrasound vibration

TABLE 3.5 Approximate Size Range Determined
by Different Methods of Particle Size Analysis

Methods of fractionation	Approximate size range (mm)
Sieving	100–0.05
Sedimentation	2<0.002
Optical Microscope	1.0–0.001
Gravity sedimentation	0.1–0.0005
Permeability	0.1–0.0001
Gas absorption	0.1–0.0001
Electron microscope	0.005–0.00001
Elutriation	0.05–0.005
Centrifugal sedimentation	0.01–0.00005
Turbidimetry	0.005–0.00005

and sedimentation. Direct sieving involves passing the dispersed soil suspension through a nest of sieves of different sizes (Appendix 3.1). The amount retained on a particular sieve represents the fraction that is larger than the sieve size on which it is retained but smaller than that of the preceding sieve. This method is primarily suited for separating coarse fractions.

The sedimentation procedure is based on the rate of fall of particles through a liquid, which depends on particle size and properties of the liquid. In 1851, G.G. Stokes developed a law that states "The resistance offered by a liquid to the fall of a rigid spherical particle varies with the radius of the particle and not with its surface."

A particle falling freely in a fluid experiences three forces: force of gravity (F_g acting downward), force of friction or resistance (F_r acting upward), and the force due to buoyancy (Fb acting upward).

$$F_g$$
$$\downarrow$$
$$\bullet$$
$$\uparrow$$
$$F_r, F_b$$
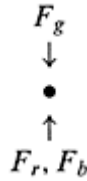
When it reaches a constant velocity, called the *terminal velocity,*

$$F_b + F_r = F_g \tag{3.1}$$

Stokes law describes the friction force

$$(F_r)\uparrow = 6\pi r\eta\theta \tag{3.2}$$

where F_r is in dynes, η is viscosity in dynes sec/cm, r is radius of the particles in cm, and θ is the terminal velocity in m/s.

The force of buoyancy (F_b) is equal to the weight of the liquid displaced [Eq. (3.3)].

$$F_b \uparrow = \frac{4}{3}\pi r^3 \rho_l g \tag{3.3}$$

The gravitational force (F_g)=volume×density×g=mg

$$F_g \downarrow = \frac{4}{3}\pi r^3 \rho_s g \tag{3.4}$$

where ρ_s is particle density (Mg/m^3), and g is acceleration due to gravity (9.81 m/s^2).

When particles attain terminal velocity, the sum of the three forces (due to gravity acting downward, buoyancy acting upward and friction acting upward) is equal to zero. The force of gravity is equal to the weight of the particle and the force due to buoyancy is proportional to the volume of water displaced. Adding a positive friction and buoyancy to a negative gravity force equals zero at a steady rate of fall.

$$6\pi r\eta\theta + \frac{4}{3}\pi r^3 \rho_l g = \frac{4}{3}\pi r^3 \rho_s g \tag{3.5}$$

Solve for θ:

$$\theta = \frac{4}{3}\pi r^3 (\rho_s - \rho_l)/6\pi\eta r \tag{3.6}$$

$$\theta = \frac{2}{9}\frac{r^2}{\eta}(\rho_s - \rho_l)g = Kr^2 \tag{3.7}$$

where K is a constant, and Eq. (3.6) is referred to as the *settling equation*. Eq. (3.6) states that the velocity of a settling particle is proportional to r^2, $(\theta\alpha r^2)$. If particles differ in their radius by a factor of 10 (2 mm versus 0.2 mm), their settling velocities differ by a factor

of 100. If the terminal velocity is attained instantly, then the time needed for a particle to fall a distance h can be calculated as follows:

$$\theta = h/t = \frac{2gr^2}{9\eta}(\rho_s - \rho_l) \tag{3.8}$$

$$\therefore t = 9h\eta/gr^2(\rho_s - \rho_l) \tag{3.9}$$

The same equation can also be solved for r if we know h and t, or for t given h and r.

$$r^2 = \frac{9h}{2t}\eta/g(\rho_s - \rho_l) \tag{3.10}$$

$$r = \frac{9}{2}\left(\frac{h\eta}{tg(\rho_s - \rho_l)}\right)^{1/2}$$

$r = A/t^{1/2}$

$$\tag{3.12}$$

$t = B/r^2$

$$\tag{3.13}$$

where A and B are constants. If V is in cm/min and d is in mm, then

$$\theta = \frac{1}{30}\frac{g(\rho_s - \rho_l)}{\eta}d^2 \tag{3.14}$$

$$d = \left(\frac{30\eta}{980(\rho_s - \rho_l)}\theta\right)^{1/2}$$

Stokes law and the settling equation are based on several assumptions. If not met, these assumptions are sources of error. Thus, the objective of laboratory experimentation is to create an experimental set-up to meet the protocols as outlined in assumptions described below.

1. The particles are large in comparison to the molecules of the liquid (> 0.0002 mm) so that the Brownian movement (colloids floating in the liquid rather than settling) does not affect their fall.
2. The fall of the particle is unhindered and not affected by the proximity of the wall. If the vessel is less than 10 times the diameter of the particle a correction is necessary:

$$\theta = \frac{2}{9\eta}r^2\frac{(\rho_s - \rho_l)}{(1 = 2.4\frac{r}{R})(1 + 3.1\frac{r}{L})} \tag{3.16a}$$

where R is the radius of the vessel, and L is the length of the vessel.
3. The particle is smooth, spherical, and rigid so that there is no *slippage* between the sphere and the medium.

4. The suspension is still and the velocity of particle is small. This means that $\theta<\eta/\rho d$. When $\theta=\eta/\rho d$ then d is called critical diameter. For ρ_s equals 2.65 Mg/m^3, critical diameter is 0.2 mm. In general, particles >0.2 mm should be fractionated by sieving.
5. Shape of the particles is critical. Rod-shaped particles are not suitable for fractionation by sedimentation. However, most soil particles are not spherical, but their diameters are computed as equivalent cylindrical diameter (e.c.d) or equivalent spherical diameter (e.s.d.).
6. The viscosity must be constant during the experiment. Therefore, temperature control is essential. The velocity of fall is about 12% faster at 30°C than at 25°C.
7. Differences in particle density may cause differences in fall velocity. Particle density can change due to hydration.

Example 3.1

Calculate the settling velocity of 0.2 mm and 0.002 mm size particles in a dilute water suspension at 20°C (units are given in Appendix 3.2 at the end of this chapter).

Solution
Substituting values of η and ρ in Eq. (3.7) and assuming ρ_s equals 2.65 Mg m^{-3} leads to the following:

$$\theta = \frac{2}{9}\frac{(1\times10^{-4}\,\text{m})^2}{(1\times10^{-3}\,\text{Kg/m/s})}\left(2.65\times10^3\,\frac{\text{Kg}}{\text{m}^3}-1.00\times10^3\,\frac{\text{Kg}}{\text{m}^3}\right)\frac{9.8\,\text{m}}{\text{s}^2}$$

$$\theta = 0.036\,\text{m s}^{-1}$$

Similarly, the settling velocity of 0.002 mm ($r=1.0\times10^{-6}$m) can be computed as follows:

$$\theta = \frac{2}{9}\frac{(1\times10^{-6}\,\text{m})^2(2.65\times10^3\,\frac{\text{Kg}}{\text{m}^3}-1.00\times10^3\,\frac{\text{Kg}}{\text{m}^3}\times9.8\,\text{m/s}}{1.00\times10^{-3}\,\text{Kg/m/s}}$$

$$\theta = 3.6\times10^{-6}\,\text{m/s}$$

Two commonly used methods of mechanical analysis by the sedimentation technique are the hydrometer method and the pipet method. For details on these methods, readers are referred to reports by Bouyoucos (1951), Day (1953), Gee and Bauder (1986), Sheldrick and Wang (1992), and Loveland and Whalley (2001).

Expression of Results of Particle Size Analysis

There are numerous methods of expression of results of particle size analyses. The data are commonly expressed as one of the following procedures.

Textural Classes. For agricultural purposes, results of mechanical analysis are expressed into different textural classes. Quantitative information on particle size distribution is used to express the data into textural classes using numerical limits or scale

for different systems, textural triangle (Fig. 3.1), and tabular values based on the textural triangle (Table 3.6).

The textural triangle has been appropriately modified for the "feel" method of textural evaluation (Ghildyal, 1988). The feel method is based on feeling the texture while rubbing moist soil between thumb and the finger. Expectedly, this is a highly subjective procedure and requires considerable experience. The procedure is, thus, extremely approximate even at its best.

Summation Curve. For engineering purposes, results of mechanical analysis are expressed in the form of a frequency diagram (Fig. 3.2) in which particle size is plotted against the percentage of the soil that falls within a
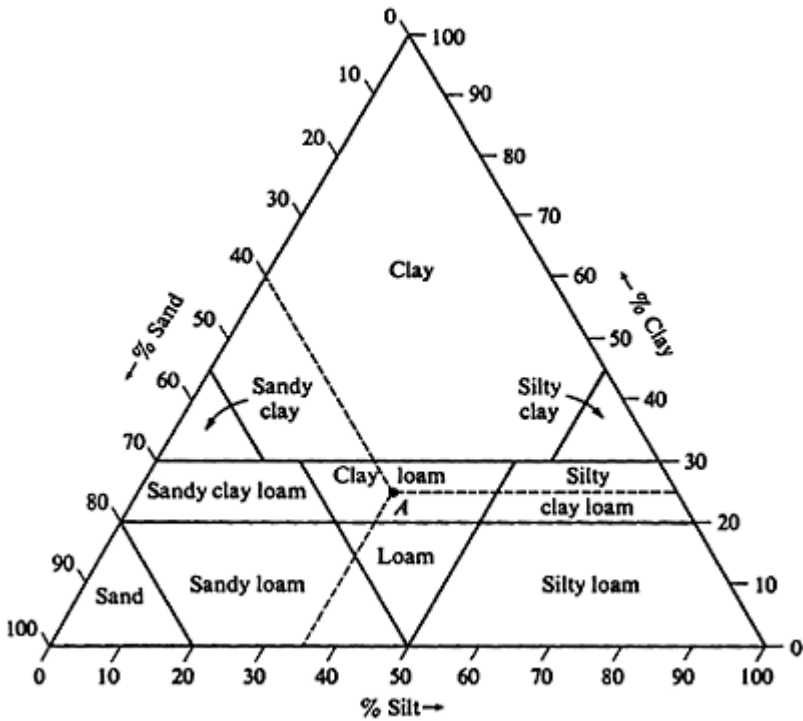

FIGURE 3.1 Textural triangle.

TABLE 3.6 Common Textural Classes Depending
on the Relative Distribution of Sand, Silt and Clay

Textural class	Soil separate ranges (%)		
	Sand	Silt	Clay
Sand	85–100	0–15	0–10
Loamy sand	91–107.	0–30	0–15
Sandy loam	40–80	0–50	0–20
Loam	23–52	28–50	7–27
Silt loam	0–50	50–88	0–27
Silt	0–20	80–100	0–12
Sandy clay loam	45–80	0–28	20–35
Clay loam	20–45	15–53	27–40
Silty clay loam	0–20	40–73	27–40
Sandy clay	45–65	0–20	35–45
Silty clay	0–20	40–60	40–60
Clay	0–45	0−40	40–100

Size distribution curve (schematics)
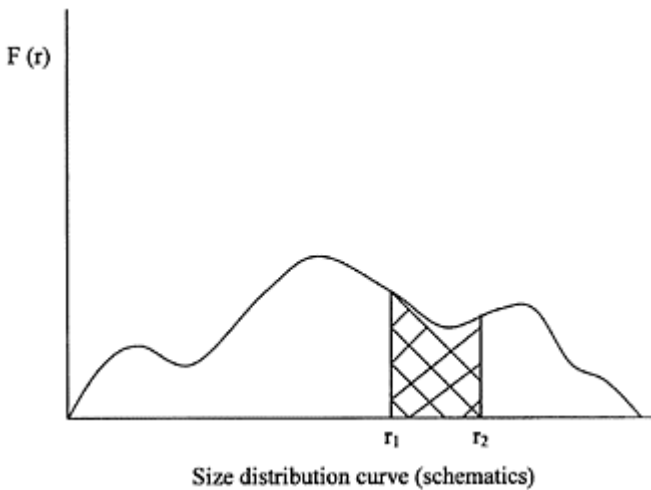
FIGURE 3.2 Frequency distribution
curve.

particular size range. Results are also plotted as summation curve or cumulative
percentage (Fig. 3.3) in which particle size is plotted against the percentage of the soil

that is smaller than a given size, and drawn as a smooth curve. The summation curve can be used to compute area under two particle diameters for characterizing different soils. Two commonly determined particle diameters are D_{10} and D_{60}, which are used by civil engineers to compute the uniformity coefficient.

   Uniformity Coefficient. For using soil as a construction material, it is appropriate to express the particle size as a coefficient or constant. Two commonly used constants by civil engineers are D_{10} and D_{60} (Table 3.7). The D_{10} refers to the diameter at 10%, which means that 10% of the soil particles are finer than this size. It is also called the *Hazen's coefficient* or the *effective diameter*. Similarly, D_{60} refers to the diameter at 60%, which means that 60% of the soil particles are finer than this size. These two constants are used to compute the *uniformity coefficient,* which is the ratio of $D_{60}:D_{10}$. The uniformity coefficient is an indicator of the uniformity of particle size. A soil with uniform particle size has a uniformity coefficient of about 1, for a soil with a wide range of particle size and $D_{60}>D_{10}$, the *uniformity coefficient* >1. Soil compactability is strongly related to the *uniformity coefficient*.

3.1.2 Particle Shape

Shape of soil particles varies widely, and often depends on the size, parent material, and degree of weathering. Coarse or large particles (e.g., sand and silt fractions) are often angular or zigzag in shape. Angularity reflects degree of weathering, highly angular particles, are less weathered and become rounded with progressive weathering by the grinding action of water and wind. In contrast, clay particles are of plate or tubular shape. Particle shape is determined by micrographs, and may be expressed using two indices:
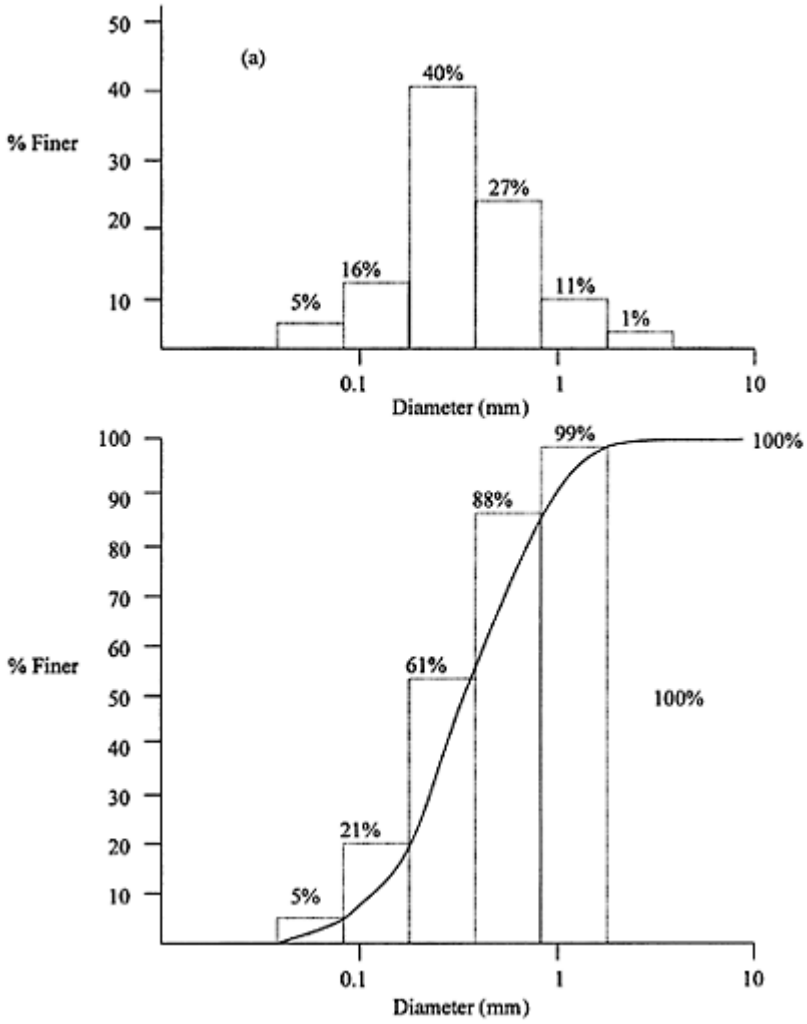
FIGURE 3.3 Summation curve.

TABLE 3.7 Computing the Uniformity Coefficient of Soil

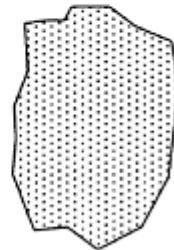| Diameter (mm)	% by weight	Summation (%)	D value
10–5	20	100	D_{100}
5–2	10	80	D_{80}
2–1	10	70	D_{70}
1–0.5	10	60	D_{60}
0.5–0.2	20	50	D_{50}
0.2–0.1	20	30	D_{30}
<0.1	10	10	D_{10}

Uniformity coefficient=D_{60}/D_{10}
D_{60}=that particle diameter for which 60% of the soil is "smaller than."
D_{10}=that particle diameter for which 10% of the soil "smaller than."
Hazen's effective size =D_{10}
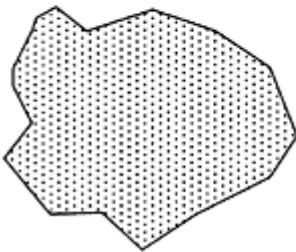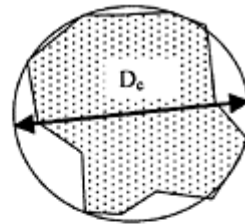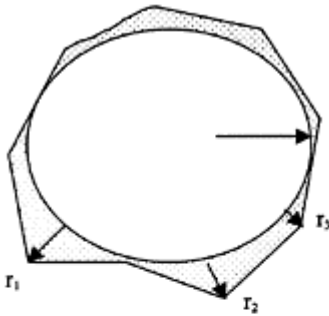
Roundness 0.44
Sphericity 0.78

Roundness 0.12
Sphericity 0.71

FIGURE 3.4 Particle shapes.

roundness and sphericity (Fig. 3.4). Roundness is a measure of the sharpness of the corner, and is computed as per Eq. (3.16b).

$$\text{Roundness} = \sum_{i=1}^{n} \frac{r_i/R}{n} \tag{3.16b}$$

where r_i is the radius of a corner, R is the radius of the maximum circle inscribed within the particle, and n is the number of corners in a particle.

Sphericity is a measure of how closely the particle approaches a sphere, and is computed as per Eq. (3.17).

Sphericity=D_d/D_c

$$\tag{3.17}$$

where D_d is the diameter of a circle with an area equal to that of the particle projection as it rests on its flat side, and D_c is the diameter of the smallest circumscribing circle. Some examples of sphericity and roundness are shown in Fig. 3.5, and other indices of particle shape are listed in Appendix 3.3 at the end of this chapter.

3.1.3 Specific Surface Area

Numerous soil properties are related to specific surface area of particles *(a)*. These properties include cation exchange capacity (CEC), retention and movement of various chemicals, swell-shrink capacity, plasticity, cohesion, and strength. Knowledge of surface area is extremely important for agricultural, industrial, and environmental applications. The specific surface area is expressed using three separate indices: surface area per unit mass *(a_m)*, per unit volume *(a_v)*, and per unit bulk volume *(a_b)* as expressed by the following equations:

$a_m = A_s/M_s (m^2/g)$

$$\tag{3.18}$$

$a_v = A_s/V_s (m^2/m^3)$

$$\tag{3.19}$$

$a_b = A_s/V_t (m^2/m^3)$

$$\tag{3.20}$$

where A_s is the total surface area, M_s is the mass of soil, V_s is the volume of soil solids, and V_t is the total volume. Surface area depends on particle size and shape. It increases logarithmically with decrease in particle size (Fig. 3.6). Plate, tubular, and chain-shaped particles have more surface area
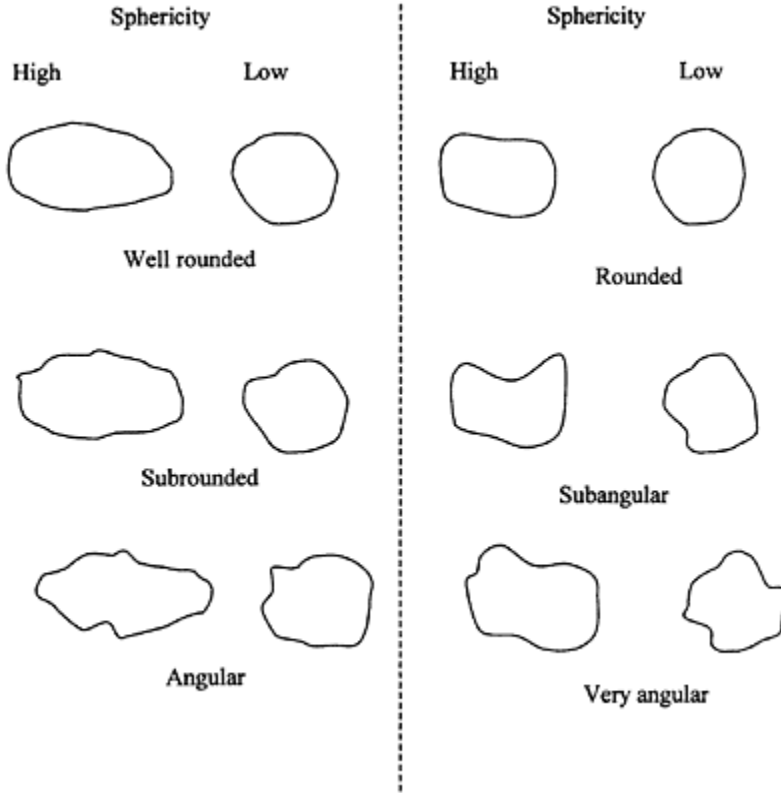
FIGURE 3.5 Soil shapes of particle sizes.

than angular or spherical particles. Surface area can be determined by the following methods.

Particle Geometry

Specific surface area can be computed assuming particle shape as follows:

A Cubic Particle. A particle of side L has a total surface area of $6L^2$, volume of L^3 and mass of $\rho_s L^3$. Therefore, specific surface area of a cubic particle is given by Eqs. (3.21) and (3.22).

$a_m=6L\ /\rho_s L=6/\rho_s L$

(3.21)

$a_v=6L^2/L^3=6/L$

(3.22)

Equations (3.21) and (3.22) show that a_m and a_v are inversely proportional to L, the smaller the particle size, the larger the specific surface area. This inverse relationship holds for all geometric shapes.
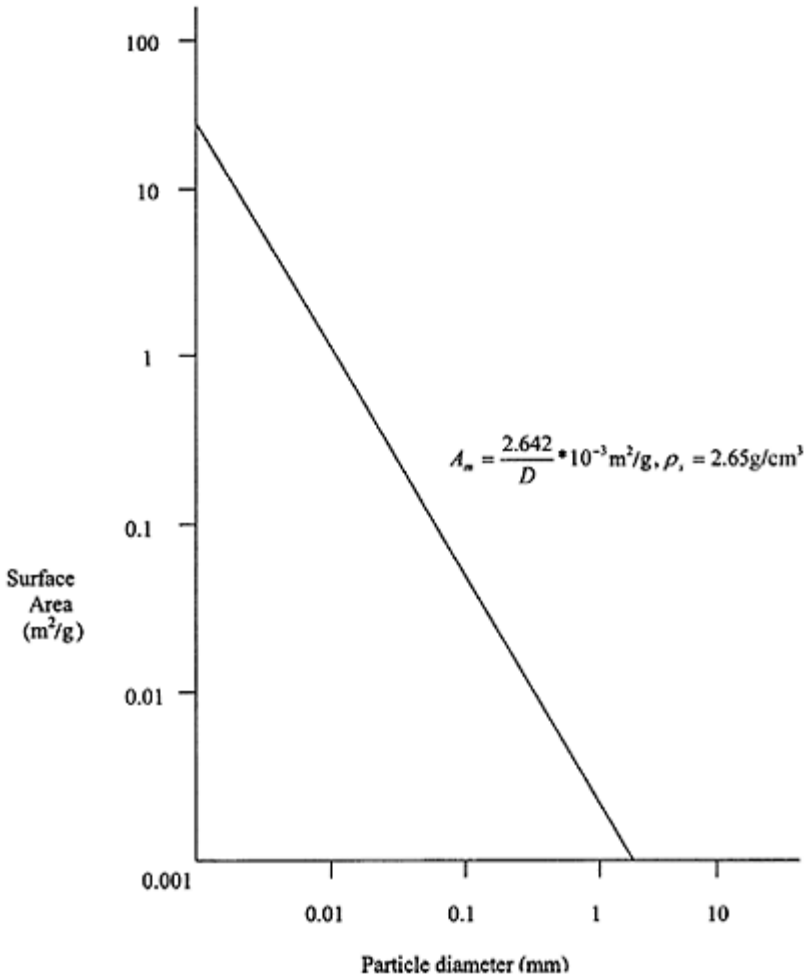

The figure shows a log-log plot with Surface Area (m²/g) on the vertical axis (ranging from 0.001 to 100) and Particle diameter (mm) on the horizontal axis (ranging from 0.01 to 10). A straight line decreases from upper left to lower right. The equation shown on the plot is:

$$A_m = \frac{2.642}{D} \cdot 10^{-3} \, m^2/g, \; \rho_s = 2.65 g/cm^3$$

FIGURE 3.6 Surface area on mass basis (A_m) decreases logarithmically with increase in particle diameter.

Spherical Particle. Specific surface area of a spherical particle is similar to that of a cubicle particle. For a spherical particle of diameter D and particle density ρ_s, the total volume is $\pi D^3/6$, mass is $\pi D^3 \cdot \rho_s/6$, and total surface area πD^2. Therefore, the specific surface area is given by Eqs. (3.23) and (3.24).

$$a_m = \pi D^2 / \frac{(\pi D^3 \cdot \rho_s)}{6} = \frac{6}{(D \cdot \rho_s)} \qquad (3.23)$$

$$a_v = \pi D^2 / \frac{(\pi D^3)}{6} = 6/D \qquad (3.24)$$

Using e.c.d. of sand (2 mm), fine sand (0.2 mm), and silt (0.002 mm), the corresponding specific surface area on volume basis (a_v) is 3×10^3 m^2/m^3, 3×10^4 m^2/m^3, 3×10^5 m^{2}m^3, respectively.

Plate-Shaped Particles with Equal Length and Width (L=b). Most clay particles are predominantly plate-shaped, and have much larger surface area, than silt and sand. Specific surface area of a plate-shaped object with length and width equal L and thickness d is given by Eq. (3.25).

$$a_v = \frac{2L^2 + 4ld}{L^2 d} = \frac{2(L + 2d)}{Ld} \ \ \text{cm}^2/\text{cm}^3 \qquad (3.25)$$

Assuming that d is negligible in comparison to /:

$a_v = 2/d$

$$\qquad (3.26)$$

Plate-Shaped Particles of Unequal Length (L_1 and L_2) and Thickness d. Total volume of such a rectangular plate is $l_1 l_2 d$, mass $l_1 l_2 d \rho s$, and total surface area $2(l_1 l_2 + dl_1 + dl_2)$. Specific surface area on mass basis is given by Eqs. (3.27) and (3.28).

$$a_m = \frac{2(L_1 L_2 + dl_1 + dl_2)}{\rho_s L_1 L_2 d} = \frac{2}{\rho_s d}\left(1 + \frac{d}{L_1} + \frac{d}{L_2}\right) \qquad (3.27)$$

$$a_v = \frac{2(L_1 L_2 + dl_1 + dl_2)}{L_1 L_2 d} = \frac{2}{d}\left(1 + \frac{d}{L_1} + \frac{d}{L_2}\right) \qquad (3.28)$$

Adsorption Isotherms

The relation between the amount of substance adsorbed and the concentration of substance in solution at any given temperature is known as the adsorption isotherm. Specific surface area of soil and other powder substances is determined from such adsorption isotherms using inert or nonreactive materials such as N_2 or ethylene glycol. The shape of the adsorption isotherm may be defined by linear $(y=mx+b)$ or nonlinear $(y=ax^b)$ mathematical function (see Chapter 16). The procedure involves monitoring the amount of gas or liquid needed to form a monomolecular layer over the entire surface. The most commonly used substances include water vapor, inert gas (N_2), or organic liquids (e.g., glycerol and ethylene glycol). A dry soil sample is saturated with ethylene glycol in a vacuum desiccator, and the excess of the polar liquid is removed under vacuum. The surface area is computed from the weight of ethylene glycol retained.

The most common approach to determining the external (nonexpanded) surface area of powders, e.g., clays, is based on the work of Brunauer, Emmett, and Teller (1938), commonly referred to as the BET method. The method assumes that nonpolar gas

molecules are adsorbed in multilayers on a solid surface, and that the amount of adsorbed gas in the initial monolayer, in contact with the surface, can be determined by constructing an adsorption isotherm and analyzing it mathematically. The BET equation was derived on the assumption that molecules in the initial monolayer, i.e., those directly on the surface, are more energetically adsorbed than molecules in all subsequent layers, and that the heat of adsorption of all layers beyond the first is equal to the latent heat of condensation of the gas. Thus, the equation theoretically differentiates the most energetically held gas molecules, and we assume that these are adsorbed in a regular array over the entire exposed solid surface.

The linear form of the BET equation is Eq. (3.29):

$$\frac{p}{x(p_0 - p)} = \frac{1}{x_m c} + \frac{c-1}{x_m c} \cdot \frac{p}{p_0} \tag{3.29}$$

where x=weight of gas adsorbed at equilibrium pressure, p=equilibrium gas pressure, p_0 = saturation vapor pressure at temperature T, x_m=weight of gas in a complete monolayer, $c=exp(E_1-L)/RT_t$, E_1=heat of adsorp-tion in the first layer, L=latent heat of condensation, R=gas constant/ mole (1,336 calories/mole), and T=absolute temperature (cgs units).

The procedure, then, is to conduct an adsorption experiment by varying p and measuring x (or v). The quantity, $p/x(p_0-p)$ is plotted against p/p_0 and this should yield a straight line with a slope of $c-1/x_m c$ and an intercept of $1/x_m c$. The amount of gas in a monolayer, x_m, is calculated by solving these two equations (from slope and intercept).

Experimental values of ethylene glycol have been found to deviate from those computed by using the BET equation given above at values of p/p_0 below 0.05 and above 0.35. Hence, useful data for surface area determinations are restricted to this range.

The total surface area of the sample is calculated from the relationship:

$$S_t = \frac{x_m}{M} \times N \times A_m \tag{3.30}$$

where S_t=total surface area (m^2), x_m=experimentally determined weight of gas in an adsorbed monolayer, M=molecular weight of the adsorbate (28.01 for N$_2$), N=Avogadro's number 6.02×10^{23}, and A_m=cross-sectional area of gas molecule in the monolayer (16.2×10^{-20}m^2 for N$_2$).

The specific surface area, a_m, is obtained by dividing the total surface area by the sample weight.

An adsorption experiment must be conducted at or below the temperature of condensation of the gas in order for significant adsorption to occur. Hence, for N$_2$ adsorption, the sample cell is immersed in liquid nitrogen (−195.8°C). The BET equation is used to calculate surface area from adsorption of nitrogen at liquid nitrogen temperatures on soil (Adamson, 1967; Greg and Sing, 1967; Shaw, 1970).

Fine-textured soils and those with high soil organic matter content have large surface areas. For further details on absorption processes with reference to Boer's law, Langmuir's equation, or BET equation refers to Sposito (1989) and Chapter 16.

3.1.4 Clay Minerals

The inorganic component consists of a wide range of minerals including crystalline and non-crystalline (Uehara and Gillman, 1981). The clay fraction primarily consists of Si, Al, Fe, H and O along with variable concentrations of Ti, Ca, Mg, Mn, K, Na, and P elements. The clay fraction is colloidal, and clay minerals are secondary minerals with significant influence on soil properties, e.g., surface area, cation exchange capacity (CEC), nutrient and water holding capacities, buffering and filtering capacity, swell-shrink properties, plasticity, compactability, and trafficability (or ability to withstand vehicular traffic). The clay minerals are hydrous aluminum silicates, with Mg^{+2} or Fe^{+3} proxying wholly or in part for the Al^{+3} in some minerals and with alkalies or alkaline earth present as essential constituents in others (Grim, 1968). Most commonly observed secondary minerals found in soil are listed in Table 3.8.

Two basic structural units are involved as building blocks in most clay minerals. The first is silicon tetrahedron, which comprises a silicon atom placed equidistant from four oxygen or hydroxyls. The silicon tetrahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$. The second unit comprises two sheets of closely packed oxygens or hydroxyls in which Al, Fe, or Mg atoms are embedded in octahedral condition, so that they are equidistant from six oxygens or hydroxyls. These two basic structures are joined together in 1:1 or 2:1 configuration to form a range of clay minerals. The lattice structure may be rigid or expanding type, and has two types of

TABLE 3.8 Commonly Observed Secondary Minerals Found in the Soil Clay Fraction

Secondary minerals	Weatherability
Geothite	Most resistant
Hematite	↓
Gibbsite	
Clay minerals	↓
Dolomite	
Calcite	
Gypsum	Least resistant

Source: Adapted from Brady and Weil 2001.

surfaces, i.e., internal and external. The total specific surface area of clay minerals, therefore, comprises internal and external surface areas. Different types of clay minerals, classified on the basis of number and arrangements of two structures, are listed in Table 3.9. There are nine principal silicate clay minerals of importance in soils. These are chloritic, glauconitic, halloysitic, illitic, kaolinitic, micaceous, montmorillonitic, sepentinitic, and vermiculitic. Predominant clay minerals present in soil affect soil

physical properties, and have a profound influence on agricultural sustainability, soil degradation, and environmental quality.

The composition of clay minerals shows that their ultimate constituents are atoms which share electrons. The atoms and their oxidation state commonly found in clay minerals along with their radii are given in Table 3.10. Atoms with similar radii can replace one another within the crystal lattice. Such type of substitution is known as isomorphic substitu-tion. This is a commonly observed process within clay minerals found in the soil.

In fact, it is this "isomorphic substitution" which leads to the formation of different types of clay minerals, and to deficit of positive or negative charge on the crystal. For example, Al^{+3} ($r=0.57$ Å) may substitute for Si^{+4} ($r=0.39$ Å) in the silicon tetrahedron unit causing a strain on the crystal structure because of the large size and producing a net negative charge deficit by one unit [Eq. (3.31)].

$$O^-S_i^{++++}O- \rightarrow O^-Al^{+++}O^-$$

(3.31)

Similarly, Mg^{+2} ($r=0.78$ Å), Fe^{+2} ($r=0.83$ Å), and Fe^{+3} ($r=0.67$ Å) may substitute for Al^{+3} in the aluminum octahedron sheet leading to charge

TABLE 3.9 Classification of the Clay Minerals

I. Amorphous

    Allophane group

II. Crystalline

    A. Two-layer type (sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)

        1.   Equidimensional

                Kaolinite group

                Kaolinite, nacrite, etc.

        2.   Elongate

                Halloysite group

    B. Three-layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer)

        1.   Expanding lattice

                a. Equidimensional

                Montmorillonite group

                Montmorillonite, sauconite, etc.

                Vermiculite

                b. Elongate

                Montmorillonite group

	Nontronite, saponite, hectorite
2.	Nonexpanding lattice
	Illite group
C.	Regular mixed-layer types (ordered stacking of alternate layers of different types) Chlorite group
D.	Chain-structure types (horneblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms)
	Attapulgite
	Sepiolite
	Palygorskite

Source: Adapted from Grim, 1968.

deficit in that sheet. In addition to isomophic substitution, broken bonds on the edges of the crystals, and ionization of hydroxyl groups attached to silicon of broken tetrahedron planes in the case of silicic acid, is also a source of charge [Eq. (3.32)].

$$Si-OH+H_2O=SiO^-+H_3O$$

$$(3.32)$$

Broken bonds and shared edges are other sources of charge on the clay particles. Consequently, clay particles have negative and positive charge on

TABLE 3.10 Radii of Ions Abundant in Common Minerals

Ion species	Symbol	Radius (Å)
Silicon	Si^{4+}	0.39
Aluminum	Al^{3+}	0.57
Ferrous iron	Fe^{+2}	0.83
Ferric iron	Fe^{3+}	0.67
Magnesium	Mg^{2+}	0.78
Calcium	Ca^{2+}	0.99
Cesium	Cs^+	1.69
Potassium	K^+	1.33
Sodium	Na^+	0.95
Lithium	Li^+	0.60
Hydroxyl	OH^-	1.40
Oxygen	O^{2-}	1.40

Chlorine	Cl^-	1.81
Fluorine	F^-	1.36

$1 \text{ Å} = 10^{-10} \text{m}.$

their surfaces, and the magnitude of charge and charge density depends on the type of clay mineral, the degree of substitution, and weathering. The positive or negative charge deficit is balanced by the absorption of anions or cations on the surface of the crystal structure. These ions are also called counter ions or gegen ions, which may be exchanged with those in the soil solution leading to anion exchange capacity (AEC) and cation exchange capacity (CEC).

Ionic bonds can be grouped into two broad categories: (i) primary or high-energy bonds, and (ii) secondary or low-energy bonds.

Primary Bonds
These are high-energy bonds and include ionic and covalent bonds.

Ionic or Electrostatic Bonds. These join two elements with incomplete outer electron shells (Fig. 3.7). These bonds involve the attraction of the unlike electrostatic charges. The atom of one element loses the electron or electrons in its outermost shell to an atom of the second element. In NaCl molecules for example, the Na atom has only one electron in its outermost shell and the Cl atom has seven. The Na atom loses its outermost electron to Cl, which completes its outermost shell. Several cations (Na^+, Ca^{+2}, Fe^{+3}, Th^{+4}, P^{+5}) and anions (Cl^{-1}, Br^{-1}, Fe^{-1}, I^{-1}, O^{-2}, S^{-2}, Se^{-2}) form ionic bonds.

Coulomb's law states that between any pairs of oppositely charged ions, there exists an attractive electrostatic force directly proportional to the product of their charges *(e₁, e₂)* and inversely proportional to the square of the distance between their centers *(D)*. The strength of the ionic bond depends on two factors: (i) the center to center spacing (interionic distance or band length) and (ii) their total charge:
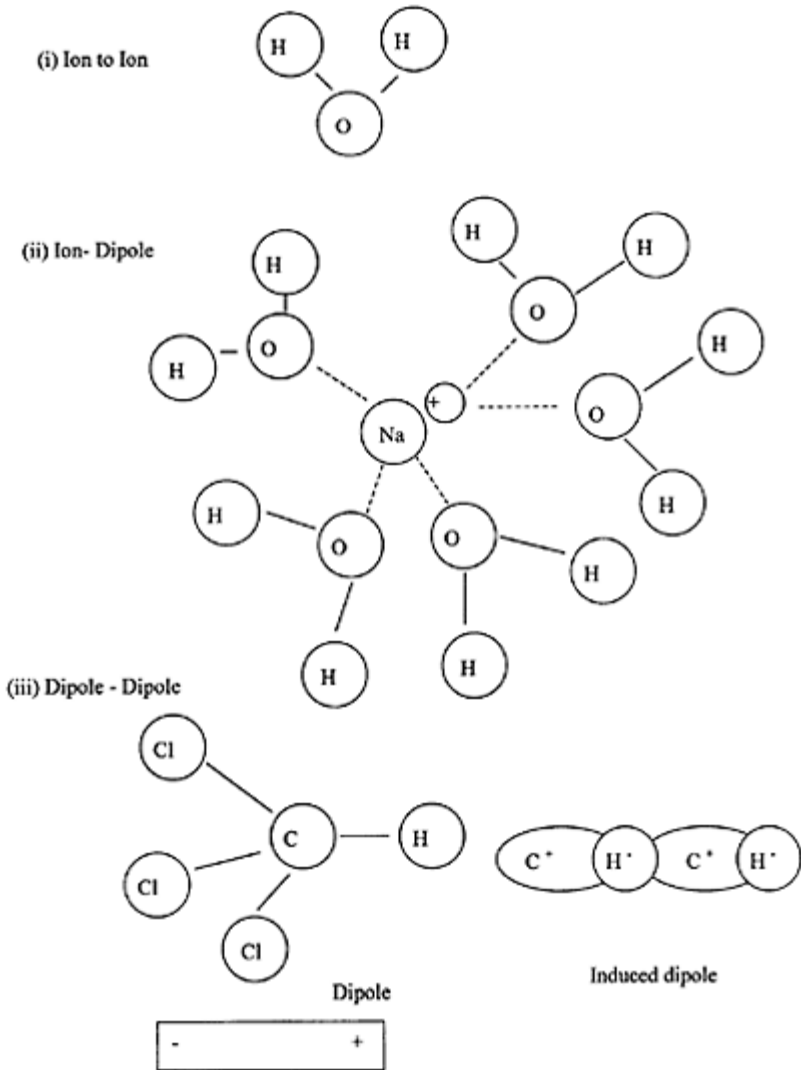
(i) Ion to Ion

(ii) Ion- Dipole

(iii) Dipole - Dipole

Dipole

Induced dipole

FIGURE 3.7 Ionic bonds (i) ion to ion, (ii) ion to dipole and (iii) dipole to dipole.

1. Two ions:

$$\text{Force of attraction} = \frac{e_1 e_2}{D^2}$$

(3.33)

2. Two dipoles:

$$\text{Dipole moment } M = ed$$

(3.34)

$$\text{Force of attraction} = \frac{2M^2}{D^2} \cdot \frac{3D^2 - d^2}{(D^2 - d^2)^2}$$

(3.35)

where d is the distance between two equal and opposite point charges *(e)* of a dipole. The ionic bond or electrostatic attraction may exist for the following combinations: (i) ion-to-ion, (ii) ion-to-dipole, and (iii) dipole-to-dipole (Fig. 3.7).

Covalent Bonds. Covalent bonds develop when two atoms are lacking one or more electrons in their outermost shell. This bond develops when one electron is shared between two adjacent atoms. These two atoms then combine by sharing the electrons in the outermost shell, i.e., the combination of two oxygen atoms forms O_2 molecule (Fig. 3.8). A single covalent bond is the sharing of two electrons between the two bonded atoms (example, H_2). A double-covalent bond is two pairs of electrons being shared (example, O_2). A triple-covalent bond is the sharing of three pairs of electrons. Examples of a triple bond include those between two nitrogen atoms (N_2) or two carbon atoms (C_2H_2).

Two atoms with the same electronegativity share the bonding electron pairs equally. As a result, the bonding electrons are evenly distributed between the bonded atoms. There is no accumulation of bonding electrons on any one atom and the bond dipole moment is zero. Such a covalent bond is called a "nonpolar" bond. The bond between two hydrogen as in H_2, two oxygen as in O_2, or two nitrogen like N_2 or are all nonpolar bonds.

On the other hand, if the two bonded atoms have a different electronegativity, then the bonding pairs of electrons are shared unequally. The atom with the higher electronegativity attracts the bonding electrons closer to itself. As a result, the electron distribution is unequal and a bond dipole moment is formed. For example, the single bond between hydrogen and chlorine as in HCl has the bonding pair closer to the higher electronegative atom (chlorine). As a result, the chlorine end is partially negative since the electrons are closer to the chlorine. The hydrogen end is partially positive since the bonding pair is farther from the hydrogen. This two-pole condition is called a dipole, and it generates a dipole moment that is a vector force directed toward the higher electronegative atom in the bond. Such a bond is referred to as a *polar bond*. The greater the difference in the electronegativity between the two bonded atoms, the more polar the bond. Elaborate descriptions of a variety of inter atomic bonds can be found in Gruenwald (1993).
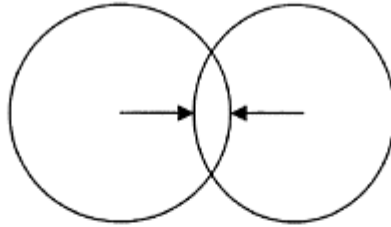
(i) A covalent bond is formed when the electron clouds of two atoms overlap.
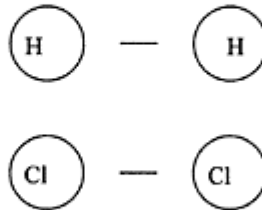
(ii) Single covalent bond. The dash is symbolic of the bonding pair.

(iii) Double covalent bond.

FIGURE 3.8 (i) Schematic of a covalent bond. A covalent bond is formed when the electron clouds of two atoms overlap, (ii) A single covalent bond. The dash is symbolic of the bonding pair, (iii) A double covalent bond.

Secondary Bonds

These are weak bonds, which include the following:

Hydrogen Bonds. A hydrogen-bond is formed when H in a H_2O molecule is attracted to the O of the neighboring molecule (Fig. 3.9). The hydrogen bond connects cation H^+ to an anion O^-, and links two H_2O molecules. This bond is weak compared with ionic and covalent bonds. In addition to water, such bonds also exist in other molecules such as NH_3. The hydrogen bond has a significant influence on soil physical properties such as
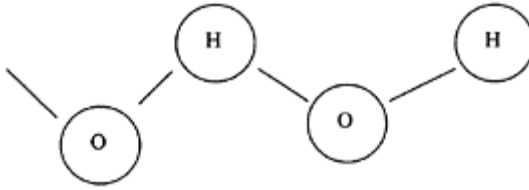
FIGURE 3.9 A hydrogen bond is formed when H in H_2O is attracted to the O of a neighboring molecule.
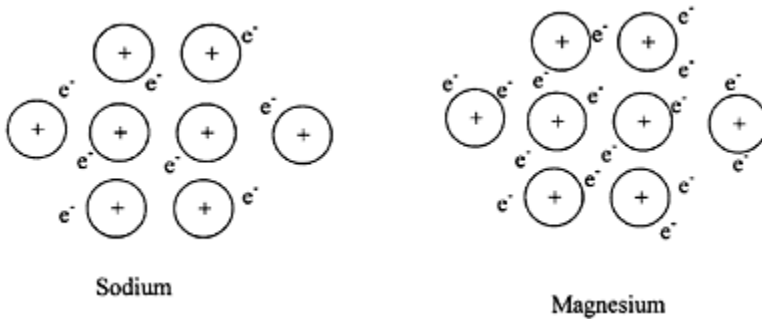

Sodium

Magnesium

FIGURE 3.10 The strength of metallic bonds increases as the number of outermost electrons increase.

heat of vaporization, dielectric constant, and infrared and ultraviolet absorption. It is because of the hydrogen bond, that the water has high boiling point and heat of vaporization.

Metallic Bonds. Metals conduct electricity because some electrons owe no allegiance to any particular nucleus and are free to drift from one nucleus to another. This type of bond is called a *metallic-bond* (Fig. 3.10).

Charge Properties of Clay

Total charge on the mineral surfaces, due to structural properties including isomorphic substitution and other alterations, is called intrinsic charge density or permanent charge. This charge is independent of soil reaction or pH. There is another variable charge, which is pH or proton-dependent, and is due to the imbalance of complexed proton and hydroxyl charges on

TABLE 3.11 Charge Properties and Specific
Surface Area of Clay Minerals

Clay mineral	Cation exchange capacity (cmol/kg)	Anion exchange capacity (cmol/kg)	Charge density [cmol(+)/ $m^2 \times 10^{-3}$]	Specific surface area (m^2/g)
Kaolinite	3–15		60–75	5–20
Illite	10–40		10–20	100–200
Vermiculite	100–150	5–10	30–33	300–500
Smectite	80–150		11–19	700–800
Allophane	20–30	10–20		>600

See Appendix 3.1 for units.

the surface. Most soils have a net negative charge, but some highly weathered soils may also have a net positive charge due to the presence of allophanes and hydrous oxides (Uehara and Gillman, 1981). The magnitude of permanent and pH dependent charge affects the amount, activity, and energy of ions absorbed on the soil surface. Some ions are more strongly attracted to the clay than others, and the ionic affinity usually follows the following order: $Al^{+3} > Ca^{+2} > Mg^{+2} > K^+ > Na^+ > Li^+$. The cation and anion exchange capacity differs among clay minerals (Table 3.11).

Electrical Double Layer and Zeta Potential
When clay particles are fully hydrated, the negative charge is balanced by the cations in the soil solution attracted by the Coulomb forces (Fig. 3.11). This negative charge on the clay surface and positive charge of the balancing cations create an electrical double layer around the clay particle (Fig. 3.12a). Three models have been proposed to explain the distribution of ion in the water layer adjacent to the clay minerals. The Helmholtz model assumes that all balancing cations are held in a fixed layer between the clay surface and the bulk solution, which is a condition of minimum energy. In contrast, the Gouy-Chapman model proposes a diffused double layer because cations possess thermal energy that causes a dynamic concentration gradient creating a diffuse double layer, which is a condition of maximum entropy (Fig. 3.12b). The third model by Stern is a combination of the two concepts, and it is a condition of minimum free energy. The double layer comprises a rigid region next to the mineral surface and a diffuse layer joining with the bulk solution. According to Stern's model, the concentration gradients are less steep in the diffuse double layer because the rigid layer lowers the surface charge (Fig. 3.12b).
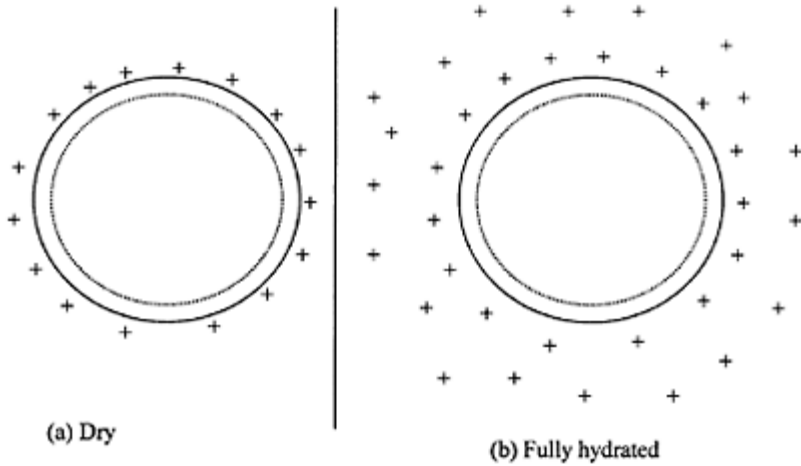
(a) Dry

(b) Fully hydrated

FIGURE 3.11 Negative charge on
clay particles: (a) dry; (b) fully
hydrated.

The cations present in the solution neutralize the negative charge on the clay particle and
the anions present in the solution. Addition of electrolytes to the system decreases the
thickness of the double layer (Fig. 3.12b).

   The Stern's double layer, therefore, comprises two parts: (i) a single ion thick layer
fixed to the solid surface and (ii) the second diffused layer, which extends to some
distance into the liquid phase. There is a potential gradient across these layers, which
comprises two components (Zeta and Nernst). The potential difference between the fixed
and freely mobile diffuse layer (or the electric potential across the double layer) is called
the zeta potential (ζ), or the electrokinetic potential (Fig. 3.12c). It is the potential
difference created at the interface upon the mutual relative movement of two phases. The
difference in the cross potentials at the interface of two phases when there is no mutual
relative motion is called the *Nernst's potential* (also called thermodynamic or the
reversible potential). The Nernst's potential does not change with addition of electrolytes
to the system, while the ζ is drastically influenced by addition of electrolytes (Fig. 3.12c).
The ζ potential can be computed as per Eq. (3.36), and the thickness of the double layer
by Eq. (3.37). Thickness of the double layer *(U)* is defined as the distance from the clay
surface at which the cation concentration reaches a uniform or a minimum value. It is the
distance over which the electrical influence of the clay platelet on its surroundings
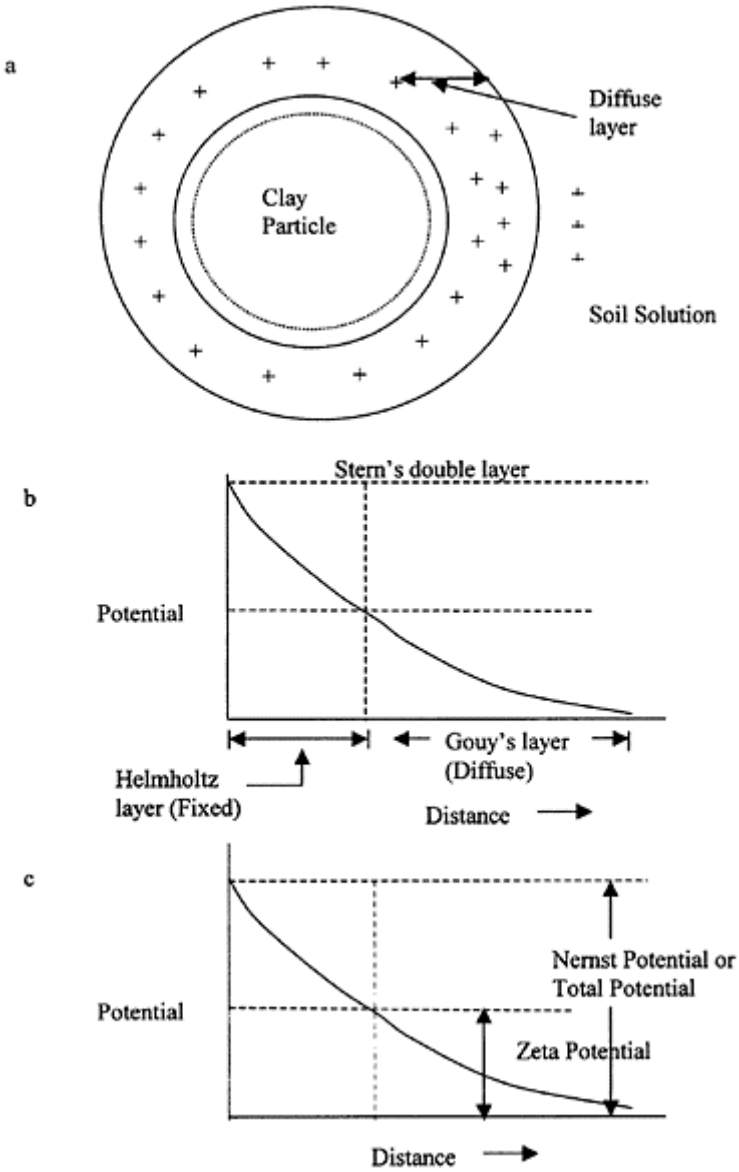vanishes.

$$\xi = \frac{u\pi ed}{\varepsilon}$$

(3.36)

FIGURE 3.12 Electric double layer
and the zeta potential.

where e (esu) is charge per cm^2, d is distance in cm within the double layer, ε is the dielectric constant of the media or permittivity (esu^2/dynes·cm^2).

$$U = \left(\frac{\varepsilon K_B T}{8 \pi C e^2 V^2} \right)^{1/2}$$

where U is double layer thickness, ε is dielectric constant, K_B is the Boltzmann constant, T is absolute temperature in K, C is counter ion concentration, e is charge per cm^2, and V is counter ion valency. U is inversely proportional to V and C. The Boltzmann constant is given by Eq. (3.38).

$$K_B = \frac{R}{A} = \frac{8.31 \text{ J/K/mol}}{6.022 \times 10^{23} \text{/mol}} \tag{3.38}$$

where R is the gas constant and A is the Avogadro's number.

Stability of Clay Suspension

The colloidal system involves dispersion in H_2O. A dispersed system involves suspension of soil particles or separates in a dilute mixture of soil in water (Fig. 3.13). Flocculation or coagulation is sticking together of colloidal soil particles in the form of loose and irregular clusters called floccules (Van Olphen, 1963; Hunter, 1987; Gregory, 1989). The process of flocculation or condensation occurs when charged colloidal particles collide with one another and adhere after the collision as a result of favorable conditions in the electrical double layer. Floccules are loose combinations of clay colloids where the original particles can be recognized. The reverse of flocculation is called deflocculation, dispersion, or peptization. The dispersion can be achieved chemically (e.g., addition of sodium hexametaphosphate to soil), or mechanically, by stirring or ultrasound vibration. The dispersity (or ability of a cation to break down the floccules and bring colloids into suspension) of the system follows the lyotropic series, which is based in part on valency of the cations [Eq. (3.39)].

Dispersity $= Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$$\tag{3.39}$$

The DLVO (Derjaguin and Landau, 1941, and Ver Wey and Overbeek, 1948) theory of colloid stability states that dispersion or flocculation depends on the net effect of van der Waals forces of attraction and electrical double layer forces of repulsion. The collision efficiency, the probability of agglomeration when two particles collide, is also important to stability of the colloidal system.
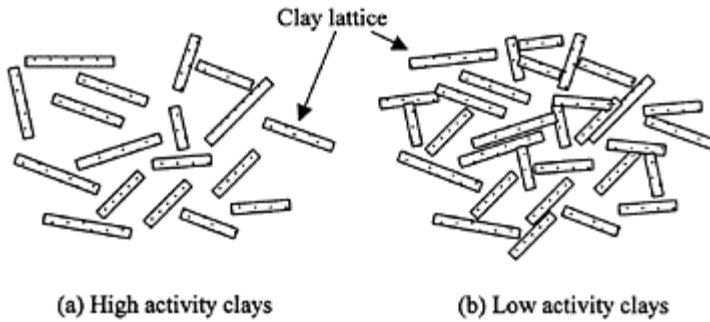
(a) High activity clays   (b) Low activity clays

FIGURE 3.13 Fully hydrated clay particles are completely dispersed. The distance between charged particles may be greater for (a) high activity clays (montmorillonite, vermiculite) than (b) low activity clays (kaolinite).

Lowering the ζ and decreasing the thickness of the double layer *(U)* to a critical level by addition of electrolytes causes flocculation. A colloidal suspension is stable as long as ζ exceeds the critical limit. When ζ falls below the critical level, the stability of the suspension is lost and it flocculates. The flocculation may be reversible or irreversible depending on charge properties of the system and of the electrolytes added. Adding electrolytes in excess of a certain amount can result in a system with ζ greater than the critical level and of the opposite sign, thereby reversing the flocculation and restabilizing the colloidal system. The effectiveness of the cation in causing flocculation depends on their valency. The higher the valency of the cation, the lower the concentration of the solution is required to reduce the ζ to the critical level. The effectiveness of monovalent, bivalent, and polyvalent cations is shown in Eqs. (3.40)–(3.42). Monovalent cations:

$$H^+ > C_s^+ > K^+ > Na^+ > Li^+$$

$$(3.40)$$

Bivalent cations:
$$Ba^{+2} > Ca^{+2} > Mg^{+2}$$

$$(3.41)$$

Polyvalent cations:
$$Th^{+4} > Al{+}^3 > Ca^{+2} > Mg^{+2}$$

$$(3.42)$$

Dispersion agents (e.g., sodium hexametaphosphate) are added during the mechanical analysis to increase ζ so that the colloidal suspension is stable and does not flocculate. In contrast, addition of lime to alkaline soil lowers the ζ so that soil can flocculate and enhance formation of aggregates.
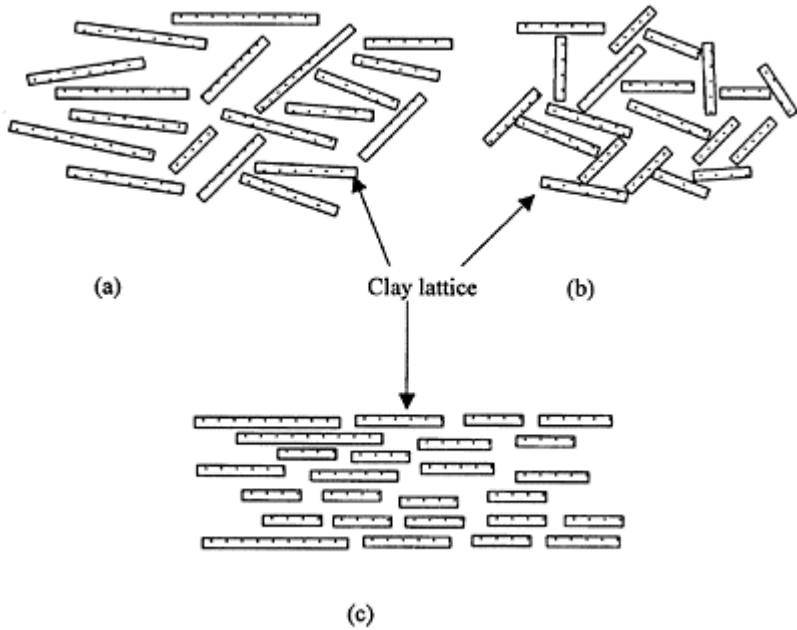
FIGURE 3.14 Decrease in zeta
potential leads to flocculation of clay
with different geometric arrangements:
(a) partial flocculation, (b) complete
flocculation with a card-house
structure, and (c) complete flocculation
with a plate condensation structure.

. Aggregation, formation of stable soil structure, is flocculation plus cementation by different cementing agents, typically inorganic plus organic matter (see Chapter 4).

Floccules are formed by a decrease in ζ potential because of the presence of ions in the solution. There are different types of flocculation (Fig. 3.14). Fully dispersed clay particles are farther apart in case of high activity (e.g., montmorillonite) than low activity (e.g., kaolinite) clays.

Incomplete Flocculation. Presence of monovalent cations (e.g., K^+) or dilute solution of bivalent cations (e.g., Mg^{+2}) can cause either weak or incomplete flocculation. Further, floccules are unstable and may set in suspension with a minor perturbation.

Random Flocculation. Rather than the plate condensation, flocculation may involve contact at the edges in a random fashion. This "cardhouse" or "brush-heap" structure of floccules is less stable (see Chapter 4).

Plate Condensation. The cations or ions added to the system are forced/aligned between the two clay crystals, and the distance between the adjoining clay particles is drastically reduced (see Chapter 4). The negative charge on the clay is neutralized by the positive charge of the cations, creating a very strong bond between them. The bond is

generally stronger with polyvalent than monovalent cations, and the bond strength follows the order shown in Eq. (3.42).

3.1.5 Swelling and Shrinkage

At low soil moisture content, clay particles are only partially hydrated. Consequently, the double layer is not fully extended and is truncated. Such a truncated double layer has a relatively higher ionic concentration than when the double layer is extended under fully hydrated conditions. Such a system, therefore, has the capacity to absorb water (a polar liquid). Increase in soil moisture content extends the double layer. Swelling is the increase in soil volume due to the absorption of water and other polar liquids. The ratio of swelling caused by a polar to a nonpolar liquid is "swelling index." A swelling system can exert pressure called "swelling pressure," and can be observed in a confined system.

The rate of water absorption and other polar liquids by clay depends on the nature of clay and the exchangeable cations. It is generally rapid at first, then becomes slower with time, and may continue for several days. In comparison, the system of wetting by nonpolar liquids (benzene or carbon tetrachloride) is very rapid and may take only a few minutes. Nonpolar substances do not cause swelling and can be used to measure soil porosity and pore size distribution (see Chapter 5).

The swelling capacity depends on the type of clay mineral and the nature of cations on the exchange complex (Table 3.12). The expanding lattice clay minerals swell more than the nonexpanding clay minerals, suggesting two types of swelling: (i) interlattice swelling, and (ii) interparticle swelling. The interlattice swelling is more in expanding lattice than the nonexpanding clay minerals:

Vermiculite > montmorillonite > beidellite > illite > Kaolinite
> halloysite   (3.43)
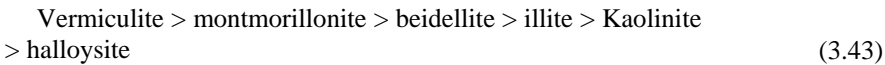
With regard to the exchangeable cations, swelling follows the order shown in Eq. (3.39). However, the order may vary with the clay mineral.

$Li^+ > Na^+ > K^+ > Ca^{+2} = Ba^{+2} > H^+$

(3.44)

This is the lyotropic series. However, H^+ does not follow the series with real soils. The specific effect of exchangeable cations on swelling depends on: (i) the number of exchangeable ions, (ii) the degree of dissociation or the

TABLE 3.12 The Relation of Swelling to the Type of Clay Mineral and Nature of Exchangeable Cations

Clay mineral	CEC (cmol/kg)	Swelling (cm^3/g colloid)					
		H^+	Li^+	Na^+	K^+	Ca^{++}	Ba^{++}
Montmorillonite (Bentonite)	95	2.20	10.77	11.08	8.55	2.50	2.50
Beidellite	65	0.81	4.97	4.02	0.50	0.91	0.85

		Swelling (cm^3/mmol cation)					
Montmorillonite	95	2.44	11.3	11.6	9.0	2.63	2.63
Beidellite	65	1.24	7.6	6.2	0.77	1.4	1.3
Ratio: Montmorillonite: Beidellite		1.97	1.49	1.87	11.68	1.88	2.02

Source: Adapted from Baver, Gardner and Gardner, 1972.

energy with which they are held, and (iii) the hydration energy of each ion determined by its hydrated radius and charge density. Both osmotic pressure and swelling increase with ionic hydration of monovalent cations.

There are two types of colloidal hydration or mechanisms involved in the swelling process: (i) water sorption and orientation on the clay surface due to the electrical properties of clay-cation-water system, and (ii) effect of cations. The former or short-range process depends on the cations, and involves van der Waals London forces, electrostatic forces, and hydration energy. The hydration energy plays an important role in the swelling process, and it overcomes the electrostatic attraction forces. During the process, the cation spacing increases significantly. These short-range forces act within the Stern layer from a distance of 10 A to about 120 A, and cause a considerable swelling pressure that may exceed 1 MPa. The swelling pressure is the force being exerted by expansion of the diffused double layer. This topic is discussed again in Chapter 8 on soil rheology. The swelling continues until the double-layer repulsive forces are balanced by attractive forces between the layer of particles, e.g., van der Waals force, positive edge-negative force attractions giving a cross-linking force [Eq. (3.45)]. It takes only a few nonparallel cross-linking particles to limit the swelling.

Hydration energy (0–10Å)+repulsion due to diffused double layer (10–120Å)=van der Waals forces+coulombic forces+cross-linking   (3.45)

Swelling due to diffused double-layer repulsion can be curtailed by strong adsorptive forces of polyvalent cations, e.g., the Coulombic attraction forces hold the two clay particles together against the double-layer repulsion.

In addition to the diffused double-layer concept, there is also a "clay domain" mechanism of swelling of clay colloids. In the dry state, clay particles are organized on a domain basis. A clay domain involves the parallel alignment of individual crystals involving a smaller volume of oriented particles. This alignment and orientation decreases the pore volume. On rewetting, domains swell as an entity, and pore volume increases proportionally to the overall volume.

3.1.6 Water Absorption on Soil Colloids

Soil's capacity to absorb water depends on its affinity for water and the antecedent temperature. The affinity for water is a function of the surface area, charge density, nature of the cations on the exchange complex, and pore size as determined by the packing arrangement. An examination of the water absorption isotherm on soil, a graphic relationship between the amount of water absorbed to the relative humidity or the vapor

pressure at a constant temperature, gives information on the relative affinity of soil for water. Soils with high clay content of expanding-lattice clay minerals and higher specific surface area have a higher affinity for water and release more heat upon wetting than soils containing low clay content and nonexpanding type clay minerals.

Two generalized water absorption isotherms are shown in Fig. 3.15. These curves can be divided into three distinct regions. Region 1 shows absorption of H_2O on exchange sites and exchangeable cations, and includes water of hydration of cations. Somewhere at the boundary between regions I and II, the monomolecular layer is complete. Soil water content corresponding to the completion of the monomolecular layer is called the *hygroscopic coefficient*. This is also the amount of soil water content at which the release of the heat of wetting is the maximum. As the vapor pressure increases, the thickness of the water film increases further and the diffuse double layer is completely expanded in the vicinity of the boundary between regions II and III. Thickness of the absorbed water film increases drastically at the relative pressure between 0.9 and 1.0, and the capillary condensation begins.

The interaction of the charges of the clay with the polar water molecules imparts to the first few adsorbed layers of water a distinct and a rigid structure. Here the water dipole assumes the orientation dictated by the charge sites on the solids. This adsorbed water may have a quasi crystalline or icelike structure, and can have a thickness of 10–20 Å or 3–7 thick layers of H_2O molecules.
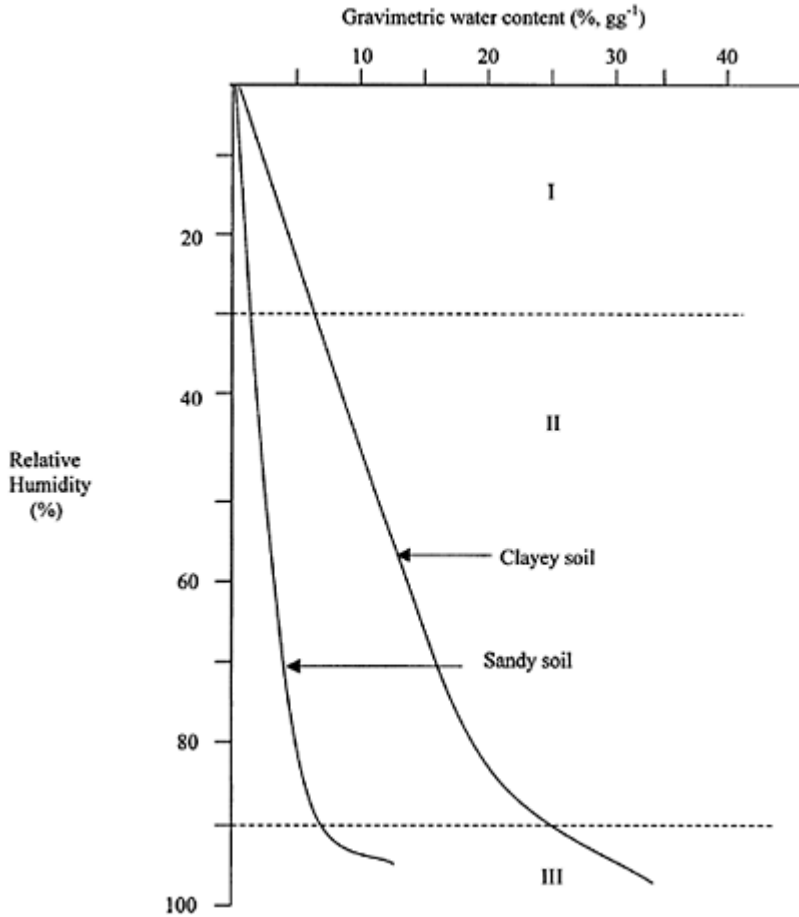
FIGURE 3.15 A schematic of water absorption on sandy and clayey soil equilibrated at different relative humidity. Three stages (I, II, III) correspond with degree of soil wetness and condensation of water in the pore.

3.1.7 Water Adsorption on Clay Surfaces and Heat of Wetting

There are several mechanisms of adsorption of water on clay surfaces (Low and Lovell, 1959). While the clay particles have a net negative charge, the water molecule is bipolar (Fig. 3.16),
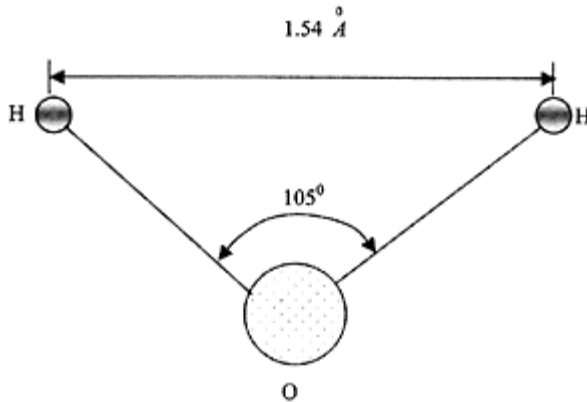
FIGURE 3.16 A water molecule showing geometic arrangment of positive and negative poles.
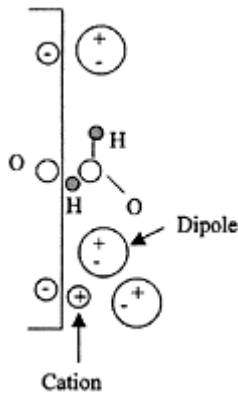

FIGURE 3.17 Adsorption of water on negatively charged clay particles.

and is able to associate with charged ions on the clay particles and in the electric double layer, and with the charge on the clay surfaces (Fig. 3.17). Water molecules associated with the cations are held as hydrated water or water of hydration (Fig. 3.18). A water molecule that attaches itself to the oxygen on clay surfaces may be held by hydrogen bonding. The H in H_2O may attach itself to the negative charge on the clay particle through electrostatic forces in which the dipole is attracted and oriented toward the negative charge on the clay surface (Fig. 3.17). The water molecule thus held to clay is called "adsorbed water," and has properties different than that of the "free water." This water is "structured" water because of the bonding to the clay surface. In comparison with the free water, the structured water: (i) has crystalline structure, (ii) is less dense, (iii) is more viscous, (iv) is less mobile,
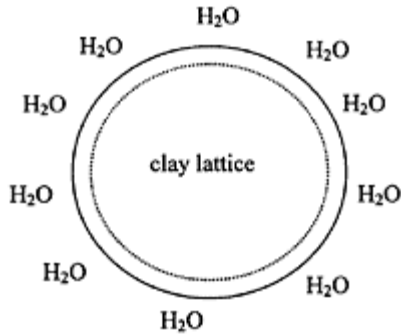
FIGURE 3.18 Water of hydration and formation of a monomolecular layer around a clay particle with moisture content equivalent to hygroscopic coefficient.

(v) has lower energy level, and (vi) has a lower freezing point. The degree of attachment of water decreases with increasing distance from the clay surface. The first layer is rather immobile, and the mobility increases in the bulk volume. The thickness of the absorbed layer differs among clay minerals, and ranges from about 8 Å in kaolinite to about 68 Å in montmorillonite.

The fixed or structured water has less energy than the free water, because the work must be done to remove the bond water. The amount of work that must be done to remove the bond water may be 3–4 Kcal per mol more than the energy released to condense vapor into the liquid state. Therefore, the energy of adsorption also differs among clay minerals.

Water adsorption on clay surfaces leads to release of energy, called "heat of wetting." The heat is also released when other liquids are adsorbed on a dry clay surface, e.g., alcohol. The heat of wetting is generally more for polar than nonpolar liquids. The heat of wetting is related to surface area. Kaolinite, with no internal surface, has a lower surface area and thus a lower heat of wetting than montmorillonite, which has both internal and external surfaces. The range of heat of wetting for some clay minerals is shown in Table 3.13.

The heat of wetting decreases with increase in water content of the clay, and varies with the nature of cations on the exchange complex. All other factors remaining the same, the heat released is generally more for divalent than monovalent cation [Eq. (3.46)]. The heat of wetting also increases with decrease in particle size, increase in surface area, and increase in CEC (Table 3.14).

$$Ca^{+2} > Mg+^2 > H^+ > Na^+ > K^+$$
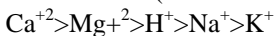
(3.46)

TABLE 3.13 Specific Surface Area and Heat of
Wetting of Some Clay Minerals

Mineral	Specific surface area (m^2/g)	Heat of wetting (cal/g)
Kaolinite	11.0–25.0	1.4–2.1
Illite (Hydrous mica)	110–250	4.8–16.5
Montmorillonite	600–800	16.5–22.2

Source: Adapted from Jury, Gardner and Gardner, 1991.

TABLE 3.14 Effect of Particle Size and CEC of
Kaolinite on Heat of Wetting

Particle size (μm)	10–20	0.5–10	0.2–4	0.1–0.5	0.5–0.25	0.25–0.10	0.10–0.05
CEC (cmol/kg)	2.4	2.6	3.58	3.76	3.88	5.43	9.50
Heat of wetting (cal/g)	0.95	0.99	1.15	1.38	1.42	1.87	—

Source: Adapted from Grim, 1968.

Heat of wetting is caused by three factors:

1. Change in state of water due to adsorption on the clay particles, or "structured water"
2. Hydration of adsorbed ions
3. Heat due to electric charge on the colloids

The orientation of adsorbed or structured water may be the cause of release of heat of wetting. The structured water is formed due to intermolecular forces. The intermolecular potential decreases as the distance from the surface decreases. If the water molecule does not react with soil colloids, the intermolecular potential energy possessed by H_2O molecules is all converted into heat. The amount of heat for adsorption of H_2O on soil can be calculated by using Eq. (3.47) (Iwata and Tabuchi, 1988).

$$\phi_m = \mu = \frac{-RT}{M} \frac{2.3 \times 0.88}{n^{1.8}} \tag{3.47}$$

where ϕ and μ are the chemical potentials of water in soil expressed in units of energy (ergs or Joules), R is gas constant (1.97cal/degree/mol), M is molecular weight of water (18 g/mole) and n is statistical number of layers of water molecule adsorbed.

The heat of hydration of ions is very large and differs among ions, being more for trivalent than bivalent, which in turn is greater than for monovalent ions. The heat of hydration is 86.0 Kcal/mol for K^+, 106.0 Kcal/mol for Na^+, 399 Kcal/mol for Ca^{+2}, 477 Kcal/mol for Mg^{+2}, and 1141 Kcal/mol for Al^{+3}. The heat of wetting of clayey soils is in large part due to the heat of hydration of cations.

The hydration of adsorbed ions is usually not complete, because these ions are bonded to the surface and not free. The partial hydration leads to only a partial release of heat of hydration. The electric charge on the soil colloids reduces the internal energy of water

molecules adsorbed by the colloid. Therefore, the heat is released when H_2O is adsorbed on the clay surfaces.

The heat of wetting can be measured by using a calorimeter or calculated from the surface tension relation as shown in Eq. (3.48).

$$\frac{U}{A} = \gamma - T\frac{\partial \gamma}{\partial T}$$

(3.48)

in which U/A is the energy per unit area, γ is the surface tension, T is the temperature in K (additional information on surface tension will be given in the section on capillarity in Chapter 11). Although heat of wetting is related to surface area, it is difficult to compute surface area of the soil from its heat of wetting because of the confounding effects of exchangeable cations and external and internal surfaces of clay minerals.

3.1.8 Packing Arrangement of Particles

Soil is a heterogenous mixture of solid particles of different sizes and shapes. It is a dynamic mixture, under continuous change due to natural (e.g., climate, biota, gravity) and anthropogenic factors (e.g., plowing, vehicular traffic). The packing arrangement of soil solids influences soil bulk density, pore size distribution and pore continuity, retention and movement of fluids, and substances contained in them (total porosity may not be affected by the packing arrangement). These properties are extremely relevant to agricultural, industrial, urban, and other land uses. Understanding the impact of packing arrangements is, therefore, important to developing and identifying systems of soil manipulation to achieve the desired configuration.

Porosity
Let's assume that a soil comprises spheres of uniform size of radius R. These spheres can be arranged into different forms of packing (Fig. 3.19). For details on different packing arrangements readers are referred to a review by Deresiewicz (1958), Yong and Warkentin (1966) and Childs (1969).