4. SOIL CHEMICAL PROPERTIES

April. 2020

4. SOIL CHEMICAL PROPERTIES

4.1. Introduction

- Soil chemical properties deal with the nature of **soil colloids** (organic and inorganic)
  - Main focuses on
    - their mineral and chemical composition
    - charges
    - exchange of ions
    - Soil reaction
    - Salinity
- The chemical properties of a soil affect
  - mineral solubility
  - nutrient availability to crop plants
  - soils ability to hold nutrients
  - a desirable chemical environment for plant growth

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4.2. MAJOR COMPONENTS OF SOIL

- soils consist of 4 major components:
  - Mineral materials, Organic matter, Water & Air
- The ideal soil (nearly loam soil), on volume basis, consists of:
  - 50% Solid State ______ (45% mineral + 5% organic material)
  - 50% pore space ______ (25% water and 25% air)
- The proportion varies greatly with depth, location, texture & other factors
  - E.g. Subsoil has ___ higher % of minerals & water
    ___ lower content of OM & air

What could be the possible reasons such subsoil composition?

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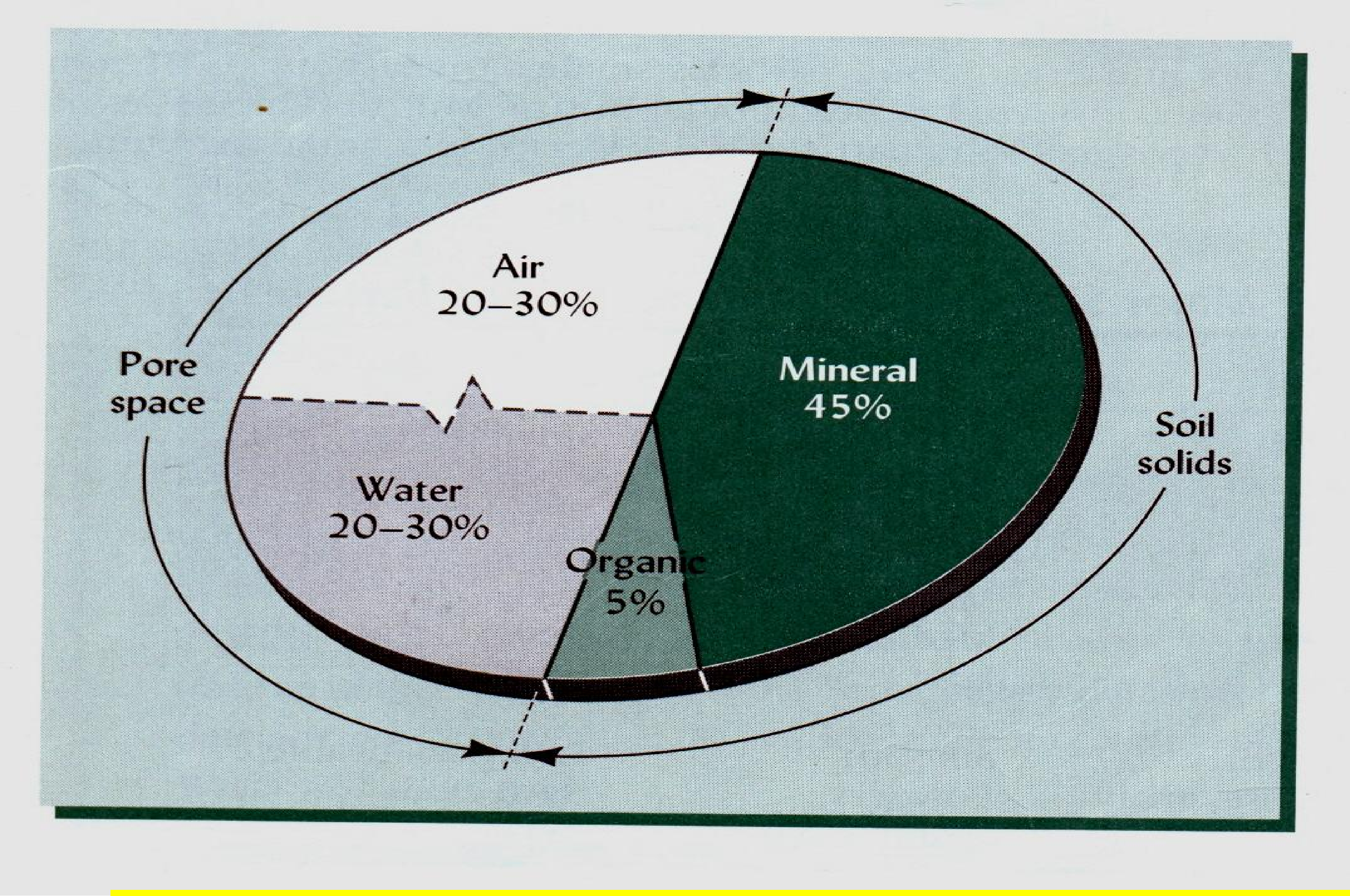

Figure : Composition of an ideal soil (by volume)

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A. MINERAL (INORGANIC) CONSTITUENT

  - Composed of small rock fragments & soil particles of various kinds
  - variable in size & composition with soil
  - can be grouped as *primary* & *secondary* minerals
- **Primary minerals**
  - Persisted with little change in composition since they were extruded in magma
  - They are prominent in the sand & silt fractions of soils

    e.g. quartz, micas & feldspars.
- **Secondary minerals**:
  - formed by the breakdown & weathering of less resistant minerals
  - These minerals tend to dominate the clay & some cases in silt

    e.g. minerals such as silicate clays , Carbonate & Oxides
- What could be basic elemental composition difference between primary & secondary minerals?

Primary minerals		Secondary minerals		
		Goethite	FeOOH	Most resistant
		Hematite	Fe_2O_3	
		Gibbsite	$Al_2O_3 \cdot 3H_2O$	
Quartz	SiO_2			
		Clay minerals	Al silicates	
Muscovite	$KAl_3Si_3O_{10}(OH)_2$			
Microcline	$KAlSi_3O_8$			
Orthoclase	$KAlSi_3O_8$			
Biotite	$KAl(Mg,Fe)_3Si_3O_{10}(OH)_2$			
Albite	$NaAlSi_3O_8$			
Hornblende[a]	$Ca_2Al_2Mg_2Fe_3Si_6O_{22}(OH)_2$			
Augite[a]	$Ca_2(Al,Fe)_4(Mg,Fe)_4Si_6O_{24}$			
Anorthite	$CaAl_2Si_2O_8$			
Olivine	$(Mg,Fe)_2SiO_4$			
		Dolomite[b]	$CaCO_3 \cdot MgCO_3$	
		Calcite[b]	$CaCO_3$	
		Gypsum	$CaSO_4 \cdot 2H_2O$	Least resistant

[a] The given formula is only approximate since the mineral is so variable in composition.

[b] In semiarid grasslands dolomite and calcite are more resistant to weathering than suggested because of low rates of carbonation weathering (see Section 2.3).

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- ***The word mineral is used in soil science in three ways***:

(1) As a general adjective to describe inorganic materials derived from rocks

(2) As a specific noun to refer to distinct minerals found in nature

E.g. quartz & feldspars

(3) As an adjective to describe chemical elements

E.g. Nitrogen, potassium & phosphorus, in their inorganic state

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B. SOIL ORGANIC MATTER (SOM)

- represents partially decayed & partially synthesized plant & animal residues
- The organic matter content of a soil is small in proportion
- However, its influence on soil properties & plant growth

C. SOIL WATER

- Soil water makes up soil solution, together with its dissolved salts
- Important as a medium for supplying nutrients to growing plants

D. SOIL AIR

- A changeable constituent, differs from atmospheric air in many aspects
- It generally contains high **relative humidity & Carbon dioxide** as compared to atmospheric air (Why?)

4.3. SOIL COLLOID

A. WHAT IS A SOIL COLLOID?

- very tiny, particles of mineral (clay) & OM (humus) dispersed in the soil matrix
- Soil colloid includes particles with diameter < 0.001mm in diameter
    - Clay fractions includes particles less than 0.002 mm in diameter
    - Therefore, all clays are not colloids

- They are most active portion of the soil, determine the properties of the soils
- Soil colloids are the sites within the soil
- ions of essential mineral such as Ca, P & S are held & protected from excessive loss
- Then, essential ions withdrawn from the colloidal bank sites & taken up by plant roots

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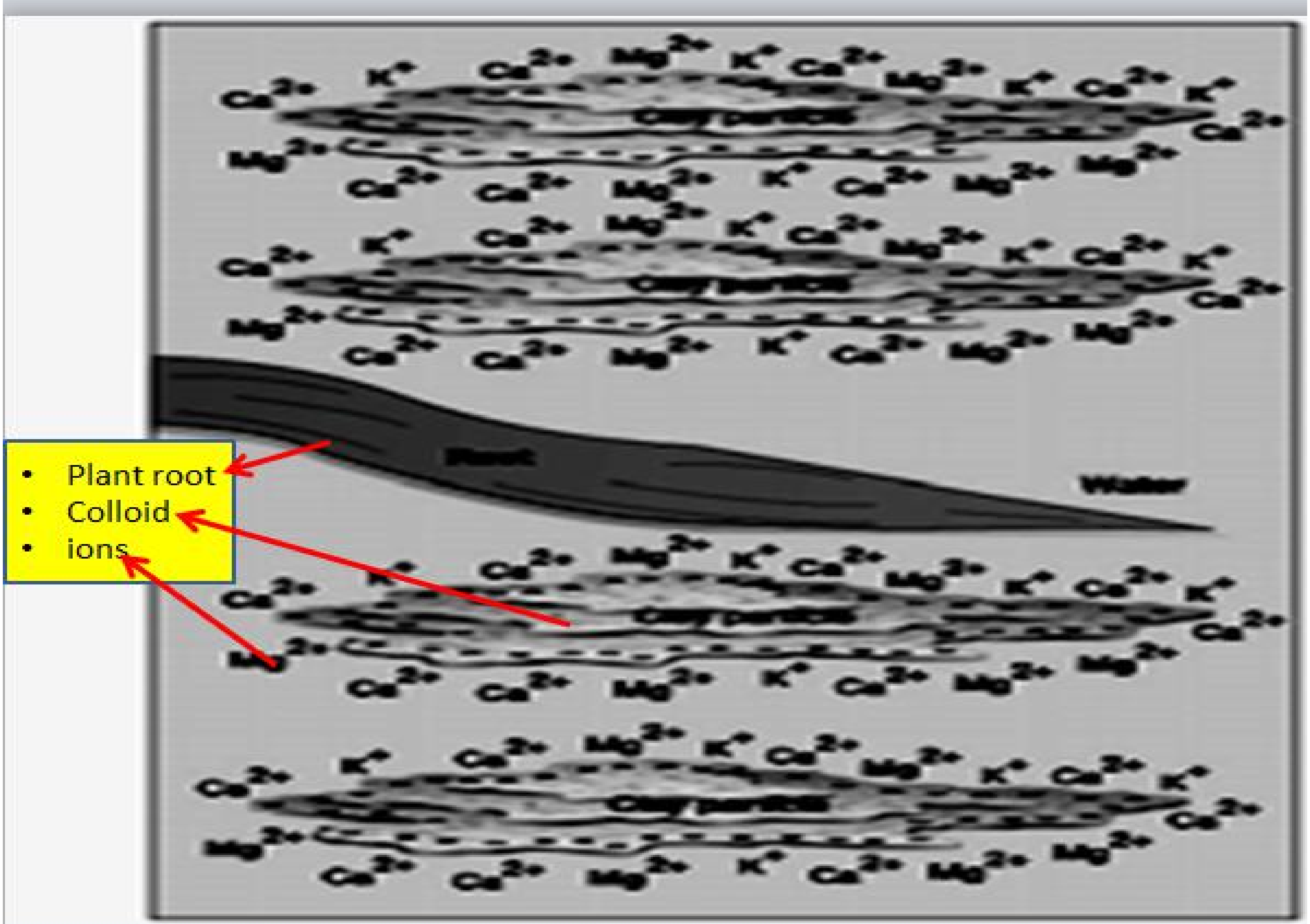

- Plant root
- Colloid
- ions

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B. GENERAL PROPERTIES OF SOIL COLLOIDS

a. Size:

- They are too small to be seen with an ordinary light microscope

b. **Surface area:**

- all soil colloids expose a large external surface per unit mass
  - *At least 1000 x about 1g of coarse sand*

- Some colloids also have excessive internal surfaces as well
    - occur b/n plate like crystal units that make up each particle
    - Greatly exceed the external surface area

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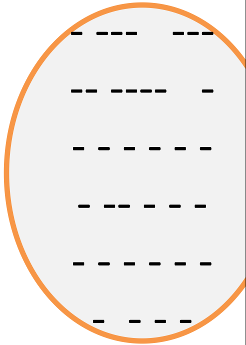
- The ***total surface area*** of soil colloids ranges from
  - 10m^2/g for clays with only external surfaces

To

  - More than 800m^2/g for clays with extensive internal surfaces

c. Surface charges



- Soil colloidal surfaces (external & internal) carry -ve &/or +ve charges
  - Most soil colloids are **negatively charges**
  - some mineral colloids in very acid soils have a net +ve charge (why?)
    - Thereby, influencing both physical & chemical properties

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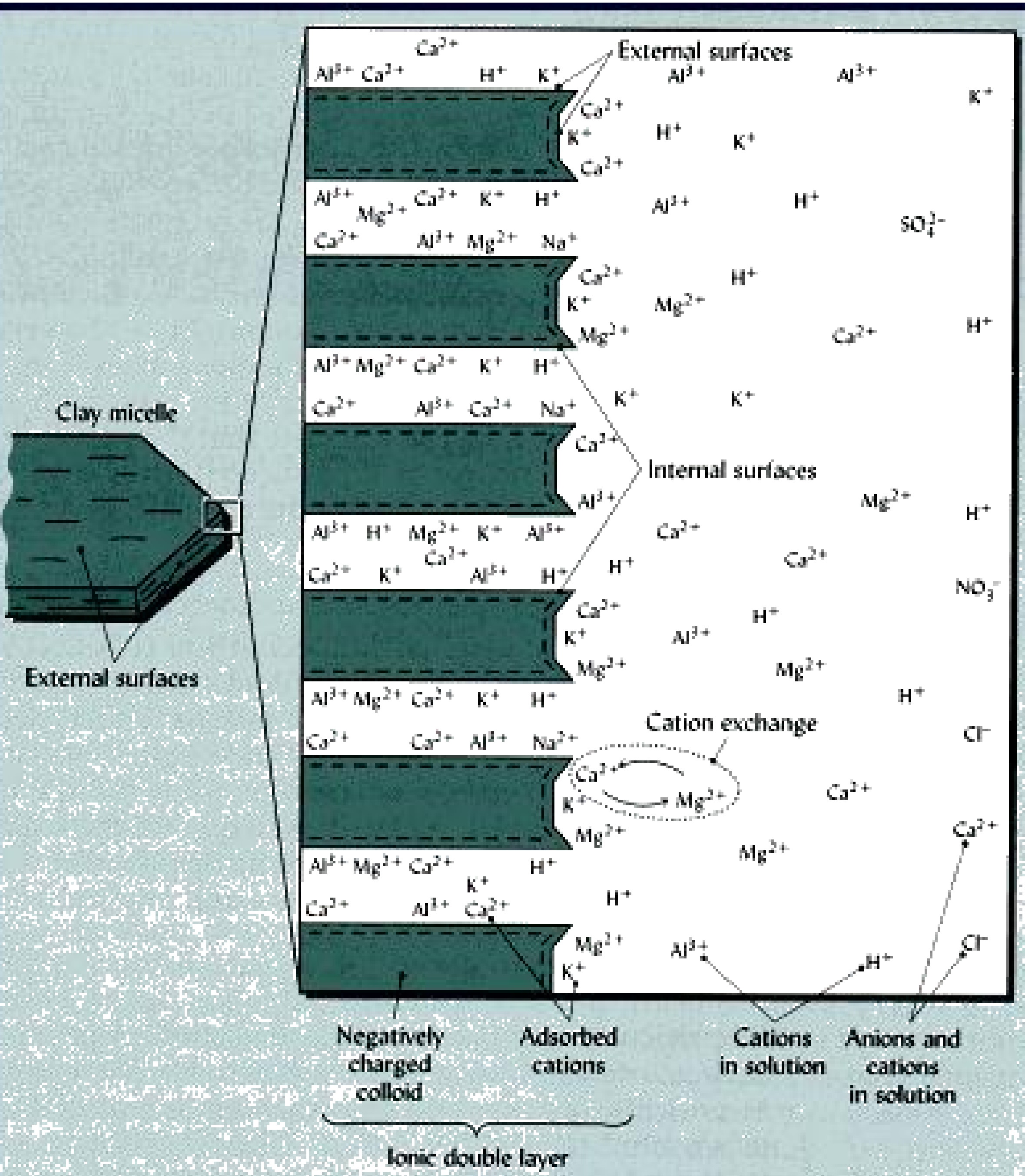
d. Adsorption of ions & water

- The charges on soil colloids attract ions of opposite charge
- The colloidal particles referred to as micelles (micro cells), attract 100 of 1000 of positive cations such as **H^+, Al^{3+}, Ca^{2+} Mg^{2+}.**
- Anions such as NO_3^-, Cl^-, SO_2^{4-} may also be adsorbed on some soil colloids

- soil colloids also attract & hold a large number of water molecules
- The charges on the internal & external colloids surfaces attract the +vely charged end of the polar water molecules

SILICATE CLAY CRYSTAL & COMPLIMENT OF IONS



C. TYPES OF SOIL COLLOIDS

- There are **4-major** types of soil colloids in soils:
    1) Layer silicates_ Crystalline Silicate Clays
    2) Allophane & associated clays_ Non-Crystalline Silicate Clays
    3) Iron & aluminium oxide clays_ oxide colloids
    4) Humus_ organic colloids

    ✓ ***Which soil colloid is better from agricultural point of views, why?***

- They can also be grouped into **two** broad categories as
    - **inorganic** (clay minerals), 1,2 & 3)
    - **organic** (humus)

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a. CRYSTALLINE SILICATE CLAYS

- Dominant inorganic colloids of most soils (except in Andisols, Oxisols, & Histosols)
- Their crystalline structure is layered much like pages in a book
- Almost all are predominantly negatively charged
- Differ widely with regard to their particle
  - Shapes
  - intensity of charge
  - stickiness,
  - plasticity & swelling
- E.g. **Kaolinite**, **fine-grained mica**, & **smectite**

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b. NON-CRYSTALLINE SILICATE CLAYS

- Consist mainly of tightly bonded O_2, Si & Al atoms
- but they do not exhibit ordered, crystalline sheets
  - E.g. **Allophone** & **imogolite**

- Most prevalent in soils developed from volcanic ashes
- Have high amounts of ____both +ve & net -ve charge

  ____high water holding capacitates

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c. IRON & ALUMINIUM OXIDES

- Occur in greater quantities in the highly weathered soils of warm humid regions

  e.g. Ultisols & Oxisols

- Examples of Iron & Aluminium oxides common in the soils are
  - **goethite** (FeOOH), **hematite** (Fe_2O_3) & **gibbsite** Al $(OH)_3$.
- Some, like gibbsite & goethite, are **crystalline structure**, but many are amorphous
- Their net charge ranges from slightly -ve to moderately +ve
- They are not sticky & plastic like the layer silicate clays
- At high pH, the particles carry a small -ve charge that is balanced by adsorbed cations
- In very acid soils, they carry a net +ve charge & attract negatively charged ions

4. SOIL CHEMICAL PROPERTIES

d. ORGANIC (HUMUS) COLLOIDS

- Humus colloids are not minerals & crystalline
- Consist of convoluted chains & rings of C- atoms bounded to H_2, O_2 & N_2
- Humus particles are often among the smallest of soil colloids
- exhibit high capacity to adsorb water
- almost no plasticity or stickiness
- has high amounts of both -ve & +ve charge per unit mass
- But the net charge is always negative & varies with soil pH
- The +ve charge on humus is high in neutral to alkaline soils

D. Fundamentals of Silicate Clay Structure

- Basic building blocks of most clay or layer silicate minerals are the **tetrahedral & octahedral sheets**

a. Tetrahedral Sheets*:*

- The basic building block for the tetrahedral sheet is a unit composed of one silicon atom surrounded by four O_2 atoms
- It is called a **tetrahedron** b/se the O_2 define the apices of a four -sided geometric solid that resembles a pyramid (having three sides the base)
- An interlocking array of such tetrahedral, each sharing its basal O_2 with its neighbour, give rise to a **tetrahedral sheet**.

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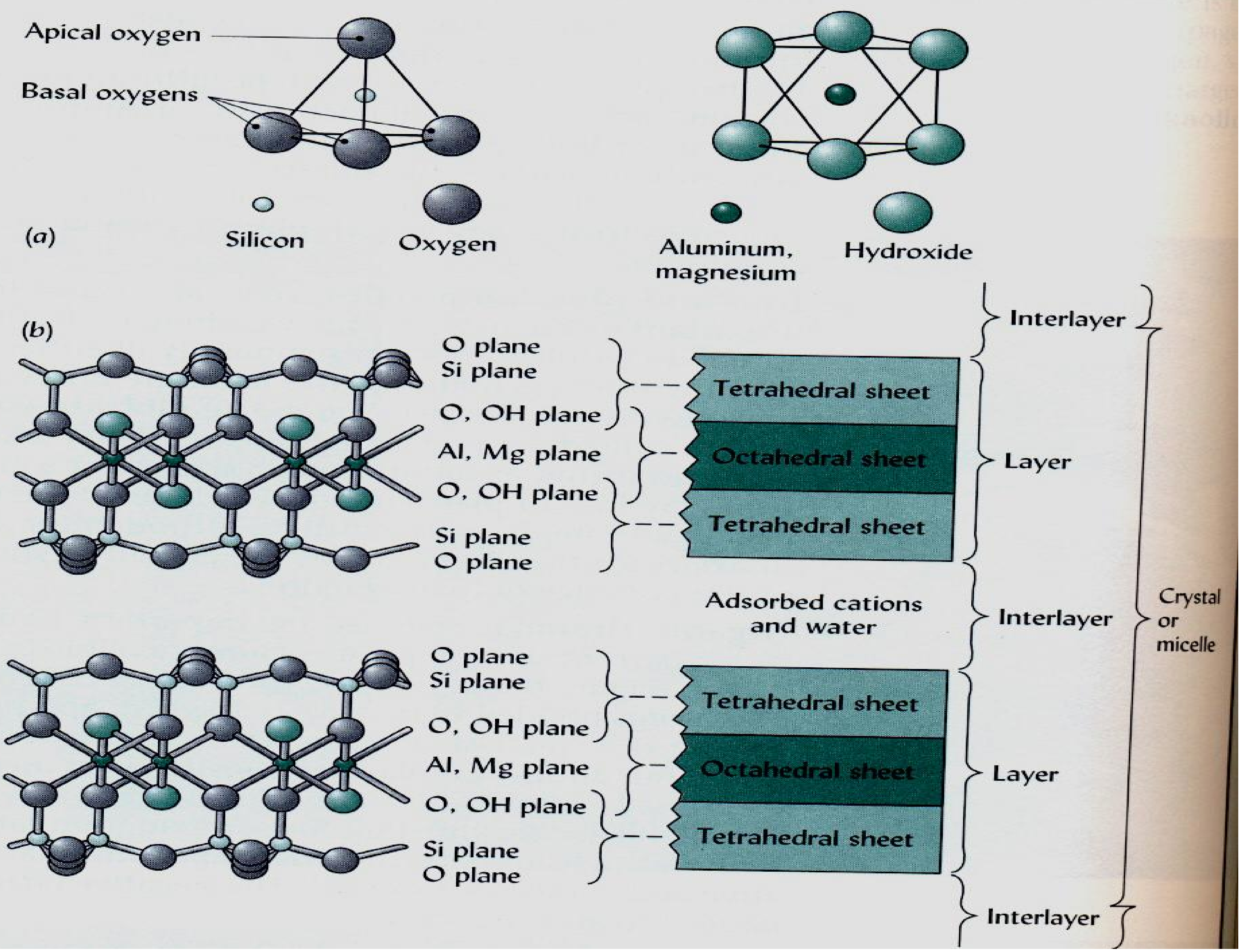
b. Octahedral Sheets:

- The building block for such kind of sheet is composed of six **O_2** atoms coordinating with a central **Al or Mg** atom
- forms the shape of an eight-sided geometric solid, or **octahedron**
- Numerous **octahedral** linked together horizontally to form the **octahedral sheet**
- If the central atom is Mg^{+2} , the sheet is called **trioctahedral** sheet
- Instead, the central atom is Al^{+3} , the sheet is called **dioctahedral** sheet

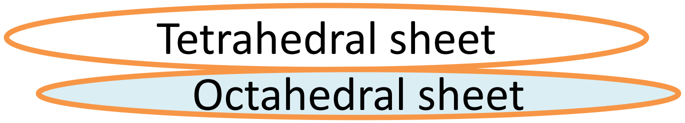

Apical oxygen
Basal oxygens
(a)
Silicon
Oxygen
Aluminum, magnesium
Hydroxide
(b)
O plane
Si plane
O, OH plane
Al, Mg plane
O, OH plane
Si plane
O plane
Tetrahedral sheet
Octahedral sheet
Tetrahedral sheet
Interlayer
Layer
Adsorbed cations and water
Interlayer
O plane
Si plane
O, OH plane
Al, Mg plane
O, OH plane
Si plane
O plane
Tetrahedral sheet
Octahedral sheet
Tetrahedral sheet
Layer
Interlayer
Crystal or micelle

Mineralogical Organization of Layer Silicate Clays

- Based on the number & arrangement of tetrahedral (Si) & octahedral (Al or Mg) sheets contained, crystalline clays classified into two main groups:

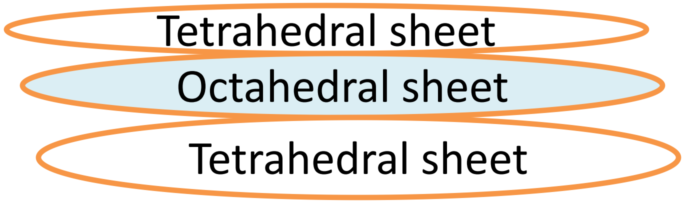
a. 1:1 silicate clays

- each layer contains one tetrahedral & one octahedral sheet



b. 2:1 silicate clays

- Each layer has one octahedral sheet sandwiched b/n two tetrahedral sheets



Features of 1:1 Type Silicate Clays

- The 1:1 silicate clays consist of one silicon tetrahedral sheet & one aluminium octahedral sheet
- The 1:1 silicate clays include **klaolinte**, halloysitc, dickite, etc.
- The sheets are held together by shared **O_2** atoms (by hydroxyl to oxygen linkage)
- Crystal units are held together by rigid H_2-bonding
- As the lattice is fixed, there is no expansion

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- they:
  - have only external surface area
  - have little isomorphic substitution
  - have low CEC (Cation exchange capacity)
  - are large in size than most other clays
  - have very low plasticity, cohesion, shrinkage, & swelling in contrast to some 2:1 type silicate clays

Features of 2:1 Type Silicate Clays

They are two kinds

1) **2:1 type Expanding**

- one octahedral sheet sandwiched b/n two tetrahedral sheets
- Expanding type minerals
  - Two of the group are **smectite** & **vermiculite**

Smectite Group

- **Montimorillonite** is the most prominent of the smectites in soils
- To a less extent,, nontronite, & saponite are also found
- The sheets are held together by shared O_2 or OH atoms
- The lattices are held together by weak **O_2 to O_2** linkages

4. SOIL CHEMICAL PROPERTIES

They:

- have expansion of crystals by H_2O entering in between
- have internal surface area
- have isomorphic substitution
- Most of the charges drives from **Mg** substituted in the **Al** positions
- some also drives from substitution of **Al for Si** in the tetrahedral sheets
- have high CEC (high negative charges)
- have high plasticity, cohesion, swelling-shrinkage

Vermiculite Group

- Octahedral sheet is **Al** dominated but in some Mg dominated
- Have considerable substitution of **Al** in the **Si** position
- high -ve charges, exceeds that of all other silicate
- Hence, have high CEC
- The **interlayer space** contain strongly adsorbed water molecules, Al-hydroxy ions & cations such as Mg
  - This hold the layer together rather driving apart
- Thus, the degree of swelling & shrinkage is **<** for vermiculites than for smectites
- For this reason, vermiculites are considered limited-expansion clays, expanding more than kaolinite, but much less than the smectites

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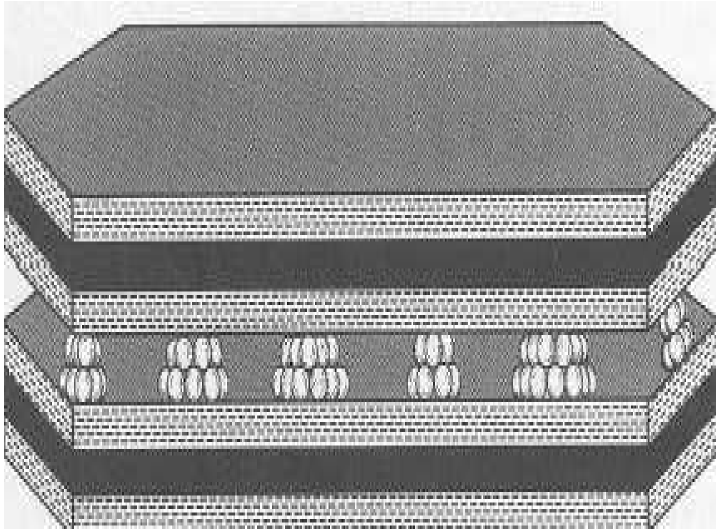

2) 2:1 type Non-expanding

- The main non-expanding 2:1 minerals are
  - **fine-grained micas** & **chlorites**

Mica Group

- The more weathered **fine-grained micas**, such as **illite** & **glaconite**, are found in the clay fractions of soils
- Unlike in smectites, the main source of charge in fine- grained micas is the substitution of **Al^{+3} in about 20% of the Si^{+4}** sites in the tetrahedral sheets
- This results in high net negative charge in the tetrahedral sheet, even higher than that found in vermiculites

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- The -ve charge attracts cations of which **K** fits the holes that exist b/n the tetrahedral **O_2** groups
- Hence, adjacent tetrahedral sheets are strongly bound together by their mutual attraction to the **K^+** in b/n
  - preventing the type of expansion that characterizes for smectite clays
- B/se of their non-expansive character, the fine-grained micas are more like **kaolinite** than smectite with regard to their
  - capacity to adsorb water
  - capacity to adsorb cations
  - degree of plasticity & stickiness

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Chlorites Group

- In the 2:1 layers of soil chlorites, **Fe or Mg**, rather than Al, occupy most of the octahedral sites
- In most chlorite clays, a **magnesium-dominated tri-octahedral hydroxide sheet** is sandwiched in between adjacent 2:1 layers
- Thus, chlorite is sometimes said to have **a 2:1:1 structure**

- Chlorites are **no expansive** b/se the **hydroxylated** surfaces of an intervening **Mg-octahedral sheet** are H_2- bonded to the O_2 atoms of the two adjacent **tetrahedral sheets**, binding the layers tightly together
- The colloidal properties of the chlorites are therefore quite similar to those of the fine-grained micas

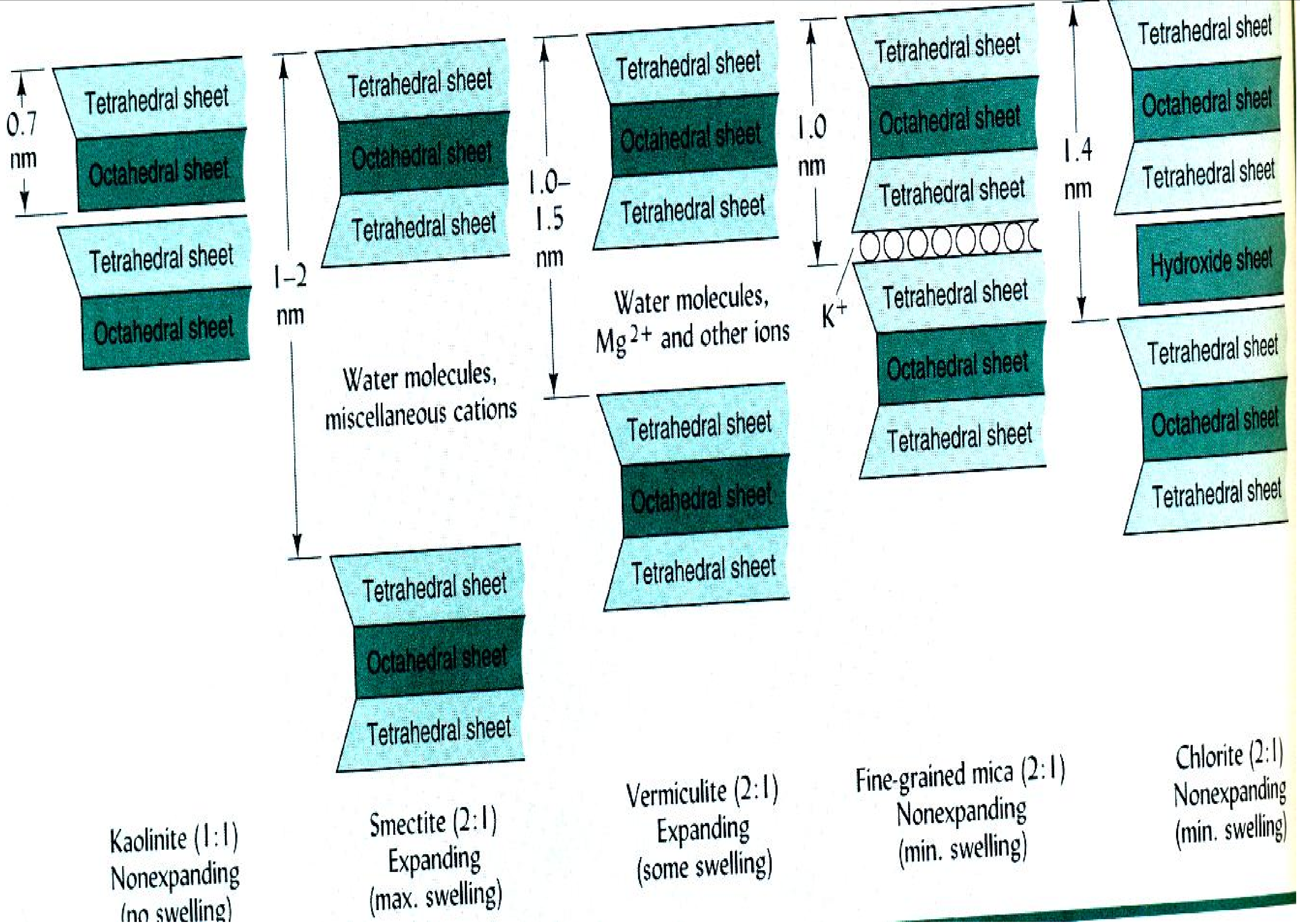
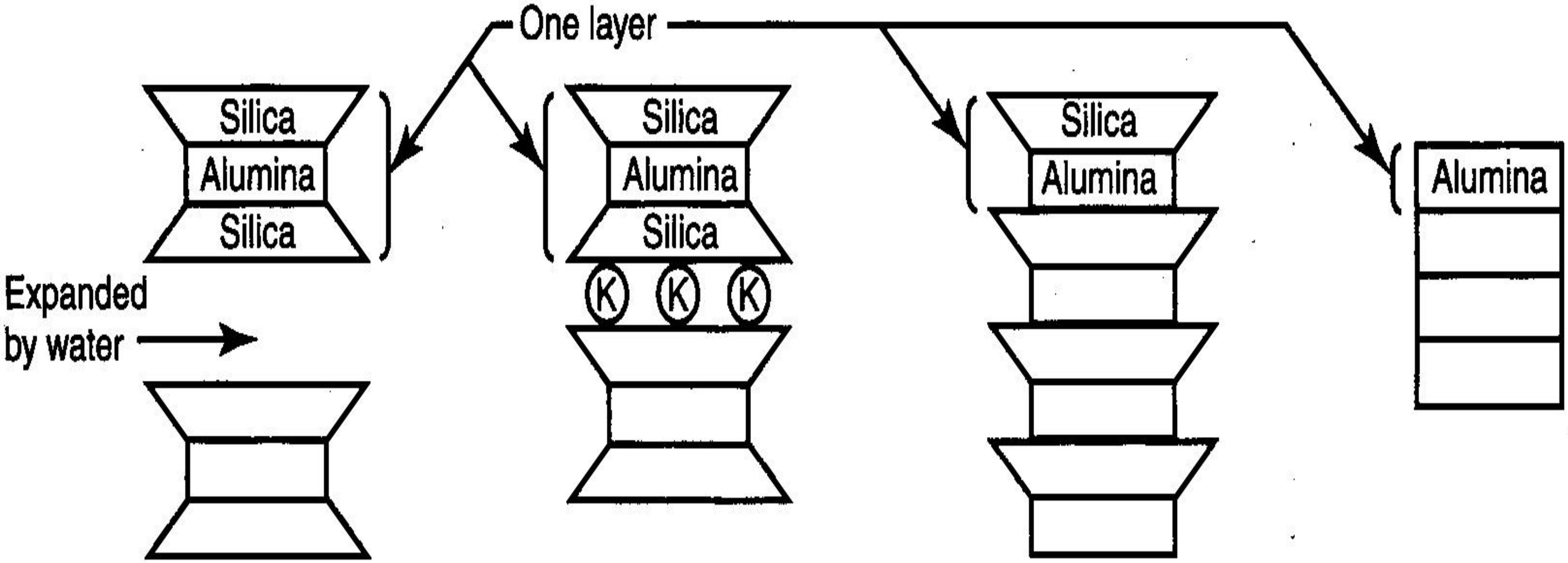


Figure .structures clay minerals



Montmorillonite
(Much expansion)

Hydrous Mica
(Slight expansion)

Kaolinite
(No expansion)

Gibbsite
(No expansion)

FIGURE 4-3 Schematic drawing of clay minerals. The lattice layers of montmorillonite within a single clay particle can be greatly expanded by water. In contrast, hydrous mica with strong bonding by potassium ions has limited swelling in some layers, probably where potassium has been removed by leaching. Kaolinite has no swelling. Sesquioxides such as gibbsite also have low or no swelling.

colloid	**type**	**Ave. CEC**	**pH dependent %**
organic	amorphous	200	90
smectite	2:1	100	5
vermicullite	2:1	150	5
Fine micas	2:1	30	20
chlorite	2:1:1	30	20
kaolinite	1:1	8	95
Gibbsite (Al)	**Non-silicate**	4	100
Geothite (Fe)	**Non-silicate**	4	100
Allophane	**Si** **Non-cystalline**	30	90

Sources of the charges on soil colloids

- Colloids are predominantly negatively charged
- This charge arises b/se of two reasons

1) Broken edges of layer silicates

- Clays have OH groups on edges, which exhibit amphoteric behaviour
- May be +vely charged at low pH & -vely charged at high pH
- This charge is variable depending on the pH of the soil solution
  - therefore called **pH dependent charge**

2. Isomorphous substitution

- Substitution of ions
    - Mg^{+2},Fe^{+2},etc for Al^{+3} in octahedral sheets, or
    - Al^{+3} for Si^{+4} in tetrahedral sheets
- Creates a net negative charge on clay particles

- This charge is fixed, and not dependent on the environment

- Since this charges are not dependent on the pH, they are termed **Permanent or constant charges**

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- Isomorphous substitution is vital b/se it is the primary source of charges
- Isomorphous substitution could be the source of both negative & positive charges
- A net negative charge is found in mineral where there has been an isomorphous substitution of a lower charge ion substitutes for a higher charge ion
- For example: Al^{+3} substitutes for Mg^{+2} in dioctahedral sheets and Al^{+3} substitutes for a Si^{+4} in a tetrahedral sheet
- Isomorphous substitution can also be a source of positive charges if the substituting cation has a higher charge than the ion for which it substitutes

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Structural Characteristics of Non Crystalline Silicate Colloids

1. Hydrous oxide clays of Fe & Al:

- These minerals occur in temperate regions mixed with others
- They are dominant in the tropics & semi-tropics
- E.g. Gibbsite ($Al_2O_3.3H_2O$), Geothite ($Fe_2O_3.3H_2O$) and Limonite **($Fe_2O_3.xH2O$)** are the most common examples of the type

- They have very low negative charges (CEC)
- Besides, they have very low stickiness & plasticity

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2. Allophone & other amorphous minerals

- Part of the hydrous oxide types in some soils are amorphous
- The same is true of part of the silica, especially in soils formed from volcanic ashes
- The most significant amorphous mineral matter in soils
    - Allophone
    - sesquioxides
- Composition approximated as $Al_2O_3.2SiO_2.H_2O$ & most prevalent in soils developed from volcanic ashes
- In most cases, properties of amorphous minerals not differ greatly from those of the crystalline minerals
- It has high CEC although it is apparently pH dependent
- Allophane also has a considerable anion exchange capacity (AEC)

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3) Organic Colloids

- Humus is an organic colloid. composed mainly of **C, H & O**
- It has very high CEC (net negative charge)
- Humus is not crystalline, having variable sizes
- Its composition and structure is complex and not well known
- ***Sources of negative charges in humus:***
- There are two sources of negative charges in humus:
- neutralized carboxylic (-COOH) and phenolic hydroxyl (OH) groups
- The charge is pH dependent. The hydrogen ion in both groups is firmly held at low pH while it easily dissociates at high pH leaving the oxygen with unsatisfied one negative charge
- Thus the number of negative charges is high at high pH & low under acidic condition

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Cation exchange & Cation Predominance

- Cation exchange is exchange of cation b/n soil solution and surface of a colloid

Major factors determine cations adsorbed by layers

1. charge strength of adsorption

- ions are not all held with equal tightness by the soil colloids
- The order of strength of adsorption when they are present in equivalent quantities is **$A^{3+} > Ca^{2+}>, Mg^{2+}>K^{+}=NH_4^{+}>Na^{+}$.**

2. concentration of the cations

- **concentration** determine the degree to which adsorption occurs
- E.g., a. in the solution of very acid soils, the conc.of **Al^{3+} & H^+** ↑
- Consequently, these ions dominate the adsorbed cations
- b. At neutral pH and above, however, the conc. of **Al^{3+} and H^+** ions in soil solution is very low
- Consequently, adsorption of these ions is ↓, rather **Ca^{2+} & Mg^{2+}** dominate
- c. In poorly drained soils, of the arid regions, salts high in **sodium** accumulate and adsorption of Na^+ becomes much more prominent

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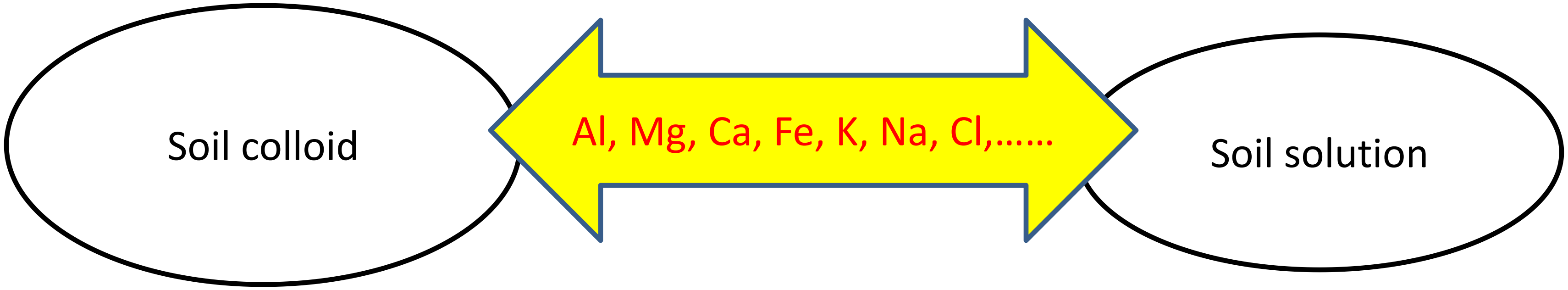
Cation Exchange Capacity (CEC)

- **CEC** is the capacity of soils to hold (adsorb) & exchange cations
- i.e. exchange of cation in soil solution with another on surface of a colloid
- It is the **quantitative measure of all the cations** adsorbed on the surface of the soil colloids
- the amount is usually expressed in terms of Cmol(+)/kg of soil.



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- The CEC is strongly affected by
    - nature, types & amount of mineral
    - amount organic colloid present in the soil

- Soils with ↑ amounts of clay & OM have ↑ CEC than sandy soils with ↓ in OM

- Soils with smectite type of clays have a ↑ CEC than soils with kaolinitic type of clays

- Soils rich in OM have ↑ CEC as organic colloids have many charged sites

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Soil reaction: Acidity and Alkalinity

- The degree of acidity or alkalinity in soils known as **soil reaction**
- It is determined by the hydrogen (H^+) ion conc. in the solution
- An acid soil has more H^+ than OH^+ ions, whereas a basic or alkaline soil contains more OH^+ than H^+ ions
- To characterize these conditions, the term soil pH is used
- A soil solution containing:
  - H^+ ions > OH^- ions is acid (acidic)
  - H^+ ions < OH^- ions is alkaline (or basic),
  - H^+ ions = OH^- ions is neutral in reaction

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- Soil reaction is expressed in terms of soil pH
- Soil pH is **the negative logarithm of the hydrogen ion** activity of a soil
- pH is given by the formula: pH= -log10 $^{[H+]}$. In the formula **"H"** stands for hydrogen ion conc. or activity

NB: pH is an indicator of soil acidity. Classes used are:

pH range	Description
<4.0	Extremely acid
4.6-5.3	Very acid
5.3-6.0	Moderately acid
6.0-7.0	Slightly acid
7.0-7.0	Neutral
7.1-8.5	Moderately alkaline
>8.5	Very alkaline

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Soil Acidity

- An acid soil has more H^+ than OH^+ ions

I. Sources of Soil Acidity

1. Removal of Ca &Mg

i. Excess removal of basic cation such as, Ca & Mg from the soil by rainfall

ii. Removal by crops

2. Addition of hydrogen

i) From the decomposition of **OM**

ii) Roots take up basic cations & exchange them with H^+

iii) Acid forming fertilizers

- **Example:** $NH^+_4 + 2O_2 \rightarrow NO^-_3 + H_2O + 2H^+$

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3. Reaction of H^+ with clay

- **The** H^+ **will cause clay particles to break down & releasing of** Al^{3+}
- Although low pH is defined as a high conc. of H^+ ions, Al^{3+} also plays a central role in soil acidity
- The exchangeable & soluble Al^{3+} ions play two critical roles in the soil acidity
- First, Al^{3+} is highly toxic to most organisms and is responsible for much of the **deleterious impact** of soil acidity on plants
- Second, Al^{+3} ions react with water (hydrolyze) to from H^+ ions
- For this reason, Al^{+3} and H^+ together are considered **acid cations**.
  - **Example:** $Al^{3+} + H_2O \rightarrow AlOH_2 + H^+$

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II. **Forms of Soil Acidity**

a. Active acidity

- Refers only to **H^+ ion activity** in the soil solution
- This pool is **very small** compared to the acidity in the exchangeable & residual pool

b. Exchangeable acidity (Salt Replaceable)

- primarily associated with **exchangeable H^+ & Al^{3+} ion** that are present in the large quantities in very acid soil
- This ions can be released in to the soil solution by cation exchange with unbuffered salt such as **KCl, $CaCl_2$ or $NaCl$**

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c. Non-exchangeable or residual acidity

- This acidity is associated **with H^+ & Al^{3+} ions** (including Al^{3+} OH)

- They are **bound in non exchangeable forms** by organic matter & clays
    - A type of acidity caused by **OM** & clays
- The residual acidity is commonly **far greater than either** the active acidity or salt replaceable acidity

Causes of soil Acidity

- **Soil acidification is a naturally occurring process which is escalate by human activity**
- **The acidification of soils is greatly accelerated by agricultural practices including:**
  - **the removal of alkaline products from farms**
  - **leaching of nitrogen from fertilizers and nitrogen fixing plants such as clovers**
  - **Leaching of basic cations**
  - **decay of plant residues**
  - **plant root exudates**
  - **inappropriate use of nitrogenous fertilizers**
  - **build up of organic matter (dissociation),**
  - **acidic parent material**

Management of Soil acidity

- **The management of acid soils should aim at**
- improving production potential by addition of **amendment to correct** the acidity
- manipulate the agricultural practices to **obtain optimum crop yields under** acid condition
- It is most important that soil acidity should be treated at an early stage
- **If acidity spreads into the sub-soil, serious yield reduction may occur**
- The first step in managing soil acidity is **to diagnose any increase** in acidity

4. SOIL CHEM...

Farming practices recommended for minimizing acidification include:

- ✓ Matching N_2-fertilizer inputs to crop demand
- ✓ Using forms of N_2-fertilizer that cause less acidification
- ✓ Efficient irrigation management to minimize leaching
- ✓ *Growing deep-rooting* perennial species to take-up nitrogen from greater depths,
- ✓ Regular applications of lime to counter the acidification inherent in the agricultural system based on soil pH, soil type and land use type
- ✓ Growing acid tolerant crop varieties such as sugarcane, coffee, papaya and bananas

Agricultural Lime Application

Soil acidity is corrected by the application of lime material

- Lime is the **cheapest and most effective** cure for soil acidity
- The carbonate component of lime consumes hydrogen ions
- The lime material has to be a **Ca or Mg salt** of a weak acid such as
  - limestone ($CaCO_3$)
  - dolomite ($Ca\,Mg\,(CO_3)_2$),
  - quicklime (CaO),
  - hydrated lime or slaked lime ($Ca\,(OH)_2$)
- In correcting acidity, enough lime should be added to neutralize not only the active acidity but also the reserve or potential acidity

4. SOIL CHEM…

- the lime requirement could be calculated using standard tables (Adams and Evans, 1962).
- **Determination of lime requirement has been also done based on acid saturation**
  It is calculated as follows:

$$\text{Acid Saturation (\%)} = \frac{\text{Exchangeable acidity (Al+ H)}}{\text{Effective CEC}} \times 100$$

Where:

Effective CEC = Exchangeable Bases (Ca + Mg + K +N a) + Exchangeable Acidity

Then:

Lime required per hectare=LRF (Ex. Acidity-(PAS x ECEC)

- Where: LRF= Lime Requirement Factor,
- Ex. Acidity= Exchangeable Acidity
- PAS= Permissible acid saturation tolerance of the crop to be sown
- ECEC= Effective Cation Exchange Capacity

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4. SOIL CHEM…

Neutral to Alkaline Soil

- In soils with pH above 7
- The **exchange complex** of these neutral to alkaline soils is dominated primarily by exchangeable **Ca^{2+}, Mg^{2+}** & other base forming cations.
- Both the aluminium hydroxyl and hydrogen ions have been largely replaced
- Most of the aluminium hydroxyl ions have been converted to gibbsite by reactions such as:
  - $\mathbf{Al(OH)_2^+ + OH^- \rightarrow Al(OH)_3}$
- The exchangeable H^+ ions are released by **base forming cations** move into the soil solution, where they react with OH^- ions to form water

4. SOIL CHEM...

- Alkaline soil (**soils** with pH > 7) should not be confused with alkali soils
- **Alkali soil** is a common name for what are now called **sodic or saline**
- **sodic soils** those with levels of Na ↑ enough to be harmful to plant **growth**
- **Current classification of alkaline (salt affected soils) includes consideration of** both pH **and** salinity measures **such as:**
  - Electrical conductivity (EC),
  - exchangeable sodium percentage (ESP),
  - the sodium adsorption ratio (SAR).

4. SOIL CHEM...

Sources of hydroxide ions

- In arid & semiarid areas, base forming cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) dominate the exchange complex of soils
- **three ways that enhance the OH^- ion conc. of the soil solution**

a. Ca^{2+}, Mg^{2+}, K^+ & Na **exchange** Al & H ions that are primary sources of H^+.

b. hydrolysis of colloids saturated with these cations release OH^- ions

c. CO_3^- & HCO_3^- if accumulate in soil offer increasing the OH ion

$$- HCO_3^- \quad + \quad H_2O \quad \rightarrow \quad H_2CO_3 \quad +$$

4. SOIL CHEM...

Alkaline soils

- Alkaline soils are found on **>1/2 of** the earth's arable lands
- dominate **most arid & semiarid** regions of the world
- significant portion is used for irrigated agriculture

- Salinity and/ or alkalinity **can be developed** when salts are naturally accumulated because of **insufficient rainfall** to wash salts from upper soil layer or **induced** by irrigation

Sources of alkalinity

- replacement of Al^{3+} & H^{+} by base forming cations
- HCO_3^{-} + CO_3^{2-} reinforce the tendency to wards alkalinity
- cation associated with CO_3^{2} also influences the pH level
- For example, **if adsorbed Na** is prominent on the colloidal complex and in the soil solution, and if ample HCO_3^{-} and CO_3^{2-} are present, $NaHCO_3$ and Na_2CO_3 will form
- Both these salts are water soluble and highly ionised,
- thus assuring continued high levels of HCO_3^{-} & CO_3^{2-} ions
- high conc. of CO_3^{2-} ions can produce pH values as high as 10 or more

4. SOIL CHEM...

Measuring Salinity & Sodicity

- Salt- affected soils adversely affect Plants
- Techniques have been developed to characterise salinity of soils
  - **pH + EC + ESP + SAR**
- Salinity is measured primarily as EC but sodicity by ESP and SAR

i) Electrical conductivity (EC):

- Pure water is a poor conductor of electricity
- conductivity increases as more and more salt is dissolved in the water.
- Thus , EC of the soil solution gives us an indirect measurement of the salt content.
- EC is expressed in terms of decisiemens per meter (ds/m

4. SOIL CHEM...

ii) Sodium status (ESP and SAR)

- The exchangeable sodium percentage (ESP) identifies the degree to which the exchange complex is saturated with sodium.

$$\mathrm{ESP} = \frac{\text{Exchangeable sodium (cmol/kg)}}{\text{Cation exchange capacity (cmol/kg)}} * 100$$

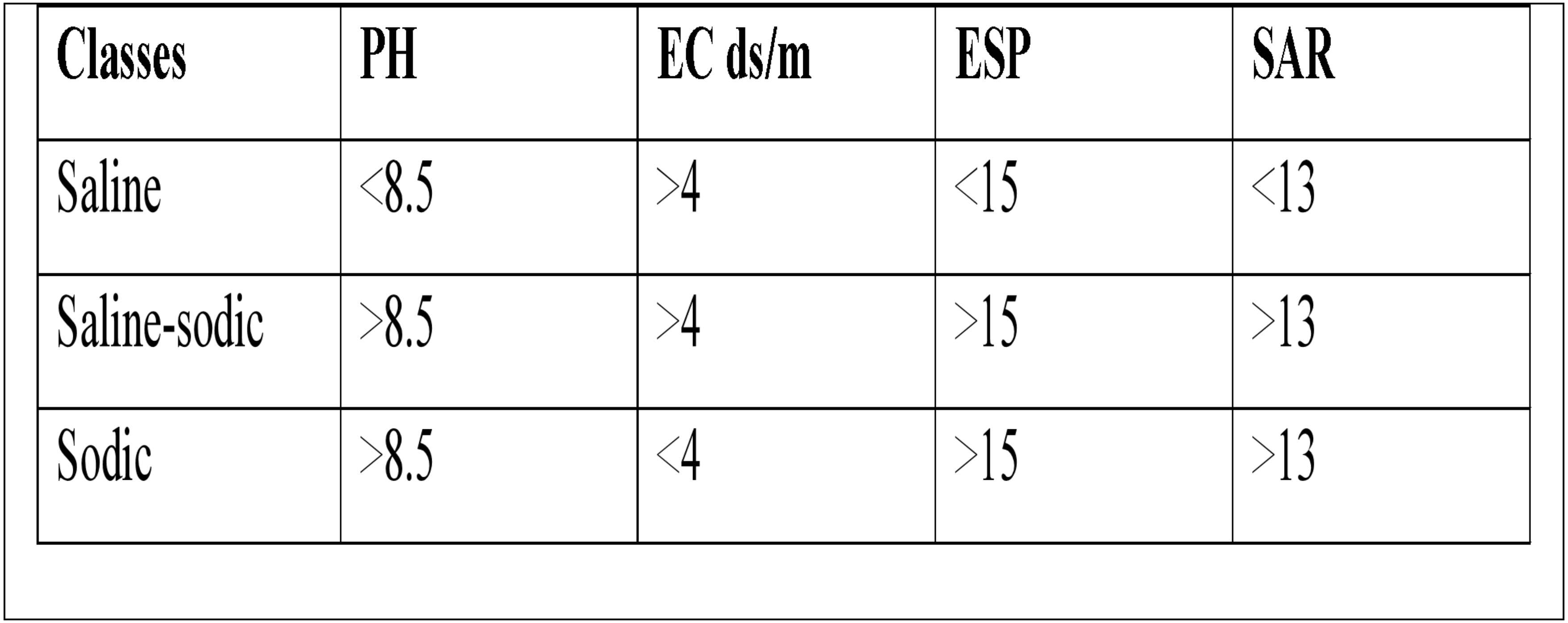
- The sodium adsorption ratio (SAR) gives information on the comparative concentration of Na^+, Ca^{2+} and Mg^{2+} in soil solutions. It is calculated as follows:

$$\mathrm{SAR} = \frac{[Na^+]}{(0.5[Ca^{2+}] + 0.5[Mg^{2+}])}$$

4. SOIL CHEM…

Classification of Salt Affected Soils

- Using EC, ESP, SAR characteristics, and soil pH, salt affected soils are classified as saline, saline-sodic & sodic.



Classes	PH	EC ds/m	ESP	SAR
Saline	<8.5	>4	<15	<13
Saline-sodic	>8.5	>4	>15	>13
Sodic	>8.5	<4	>15	>13

4. SOIL CHEM...

Saline soils

- The processes that result in the accumulation of neutral salts are referred to as salinization
- The salts are mainly Cl & SO_4 of sodium, calcium, magnesium & potassium
- Saline soils contain a concentration of these salts sufficient to interfere with the growth of many plants
- Salts are commonly brought to the soil surface by evaporating water, creating white crust,

- **Sodic soils:**
- level of neutral soluble salts is low
- level of Na is high
- high pH level is due to the hydrolysis of sodium carbonate
- Plant growth of those soils is constrained by toxicities of Na^+, and HCO_3^- ions
- As well as their very poor physical conditions & slow permeability of water

4. SOIL CHEM...

- **Saline sodic soils:**
- characteristics intermediate b/n the two
- Like saline soils they contain appreciable level of neutral soluble salts
- they have **higher ESP & SAR level**
- Crop growth can be adversely affected by both excess salts and excess sodium levels.

Q . Compare the three types of Salt Affected Soils

Significance of Soil pH in Soils & Plant Growth

- when crop plants do not grow well, one of the first questions the soil scientist usually asks is **"what is the pH of the soil"?** B/s soil pH indicates a no of soil fertility characteristics
- **soil pH has importance in soil-plant r/p b/se it determines**
    - Solubility and availability of plant nutrients
    - Lime requirement of soils
    - Activity of roots of higher plants
    - Activity of desirable soil micro organisms E.g. AOB, NOB, NFA
- **soil pH influences nutrient absorption and plant growth in two ways:**
    - Direct through the toxic effect of H^+ ion on plant root growth and development
    - Indirectly through its influencing on nutrient solubility and availability

4. SOIL CHEM...

- Generally, for agricultural purpose, soils with pH values within the range of 5.8 to 7.5 are suitable

a) Nutrient availability

In strongly acid soils

- availability of the macronutrients (Ca, Mg, P, N, S) ,Mo & B is curtailed.
- availability of the micronutrient cations (Fe, Mn, Zn, Cu, Co) is increased

In slightly to moderate alkaline soils,

- Mo & all macronutrients (except P) are sufficiently available
- level of available Fe, Mn, Zn, Cu & Co are so low
- P &B availability is like wise reduced in alkaline soil
- pH range of 5.5-6.5 or perhaps 7.0 may provide the most satisfactory levels for plant

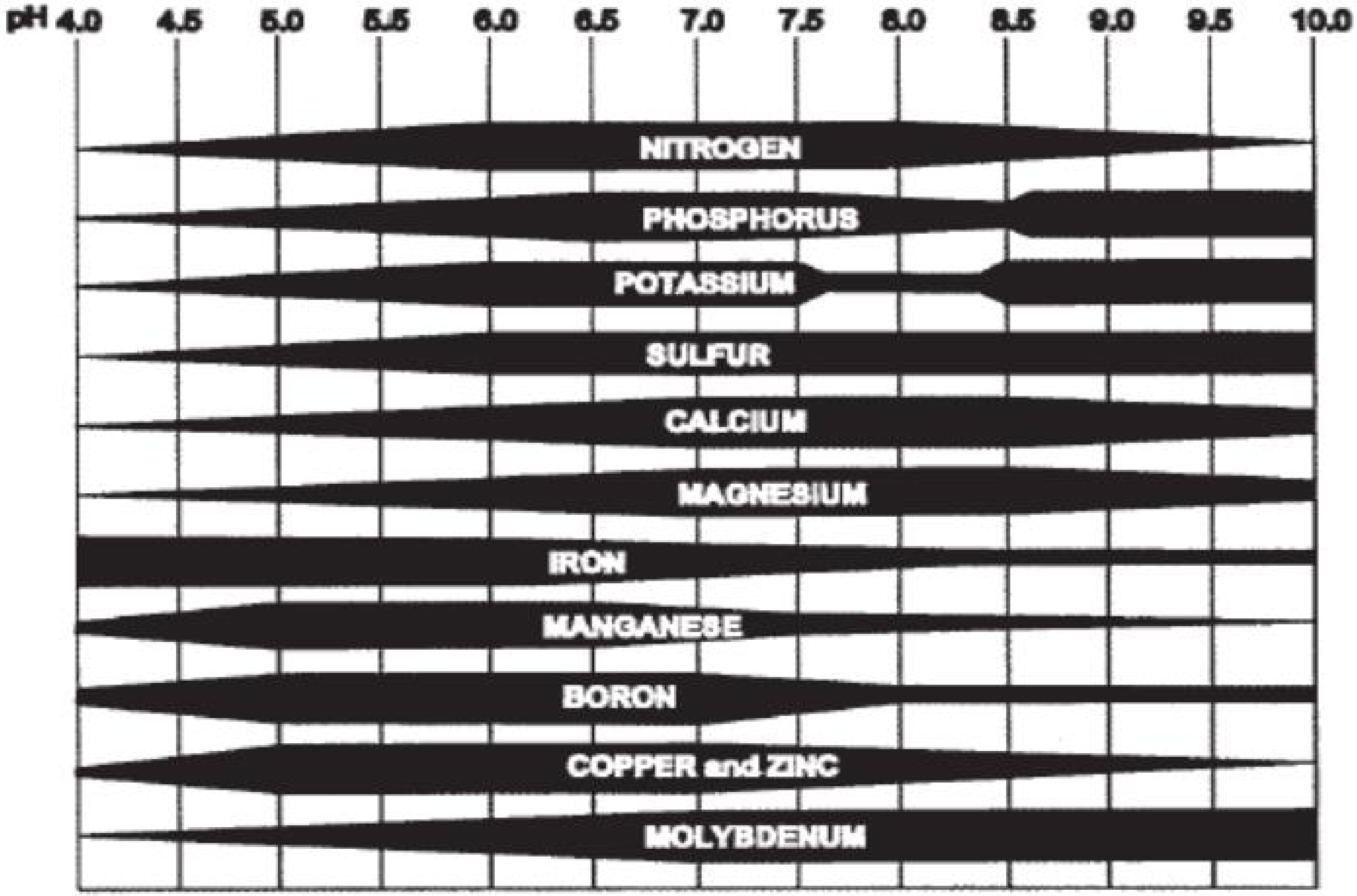


Figure. Nutrient availability at different pH vales (maximum availability is indicated by widest part of bar

4. SOIL CHEM…

b) Higher plants & soil pH:

- Plants vary in their **tolerance** to acid and/or alkaline conditions
- For example, certain legume crops such as alfalfa grow best in near neutral or alkaline soils
- most humid region mineral soils must be limed to grow this crop satisfactorily.
- Tea and coffee are at the other end of the scale
- They require considerable amount of iron, which is abundantly available at low pH values

4. SOIL CHEM…

Soil pH & Cation Associations

- The CEC of a soil increases with soil pH
- As pH moves from very acid soils to neutrality & above, the exchangeable complex dominated by exchangeable base forming cations such as Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, etc.
- However, as the pH moves from neutrality to very acid, the exchange complex is dominated by exchangeable Al^{3+} & H^{+}

Cation Saturation Percentage

- The proportion of the CEC occupied by a given ion is termed its saturation %
- The non acid cations (Ca^{2+}, Mg^{2+}, K^{+}, Na) have been refereed to as base cations their proportion on the CEC is called the **percent base saturation (PBS)** or sometimes called as **non acid saturation**

4. SOIL CHEM...

- Exchangeable Al^{+3} & H^{+} are called **acid cations** and their proportion on the CEC is called **percent acid saturation**
- The relationships among these terms can be summarized as follows

$$\mathbf{PBS} = \frac{\text{cmol}_c\text{/kg of exchangeable}(Ca^{2+} + Mg^{2+} + K^{+} + Na)}{\text{cmol}_c\text{/kg of CEC}} * 100$$

$$\mathbf{PAS} = \frac{(\text{cmol}_c\text{/kg of exchangeable } Al^{+3} + H^{+})}{\text{cmol}_c\text{/kg of CEC}} * 100$$

Percent Base Saturation (PBS)+ Percent Acid Saturation (PAS)= 100

4. SOIL CHEM...

- PBS is frequently used as an indication of soil fertility
- most of the time exchangeable Al^{+3} is detected, in the soil with pH <5.5
  - **Humid region soils are distinctly acid & about two-thirds base saturated**
- (Semi) arid region soils have pH near ($\geq$) 7 and its PBS is 100%
- H & Al in humid & Ca in semi-arid, are dominant cations on the exchange sites
- **Question**: Consider a soil with a CEC of 20 $cmol_c$/kg holding these amounts of exchangeable cations (in $cmol_c$/kg): 10 of Ca^{+2}, 3 of Mg^{+2} ,1 of Na^{+} ,1of H^{+} and 4 of Al^{+3} . Calculate the percent calcium saturation, percent aluminium saturation, Percent Base Saturation and Percent Acid Saturation