

**University of Salahaddin
College of agriculture
Dept. of Soil and Water**



**Academic year 2023-2024
second -year Students
Spring Semester**

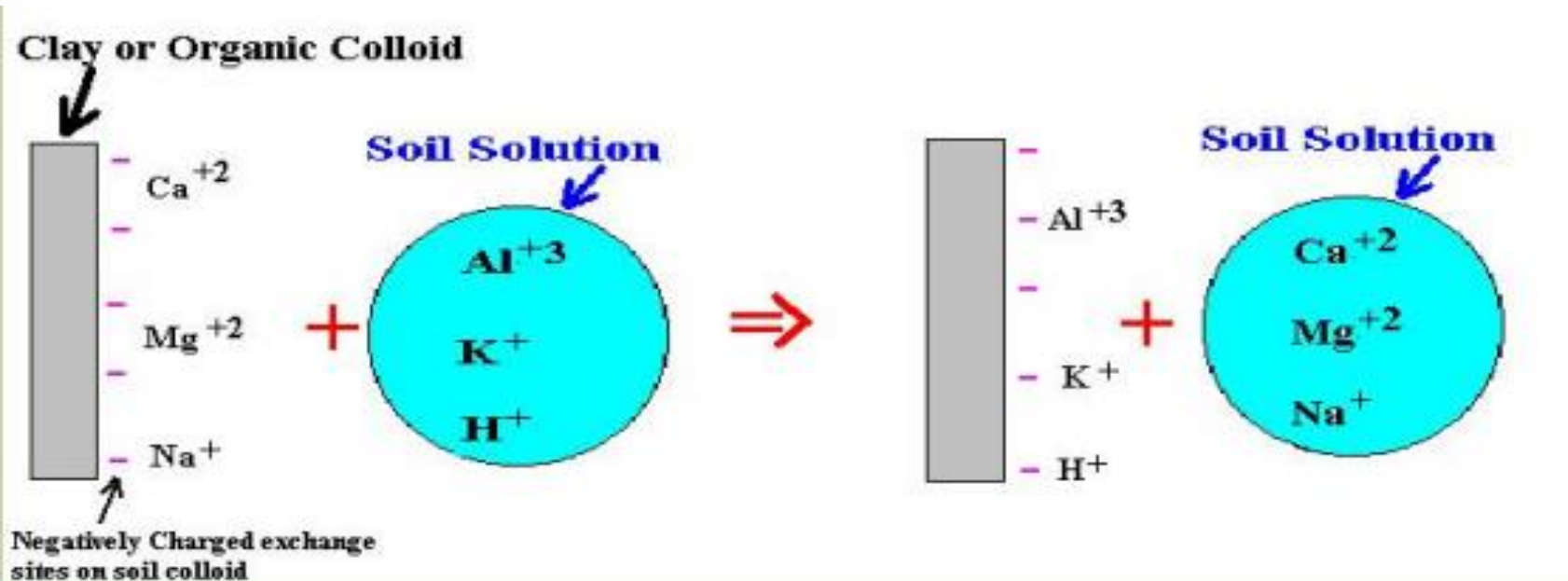
soil chemistry

L3

Dr. Kazhin Sarbaz Rajab

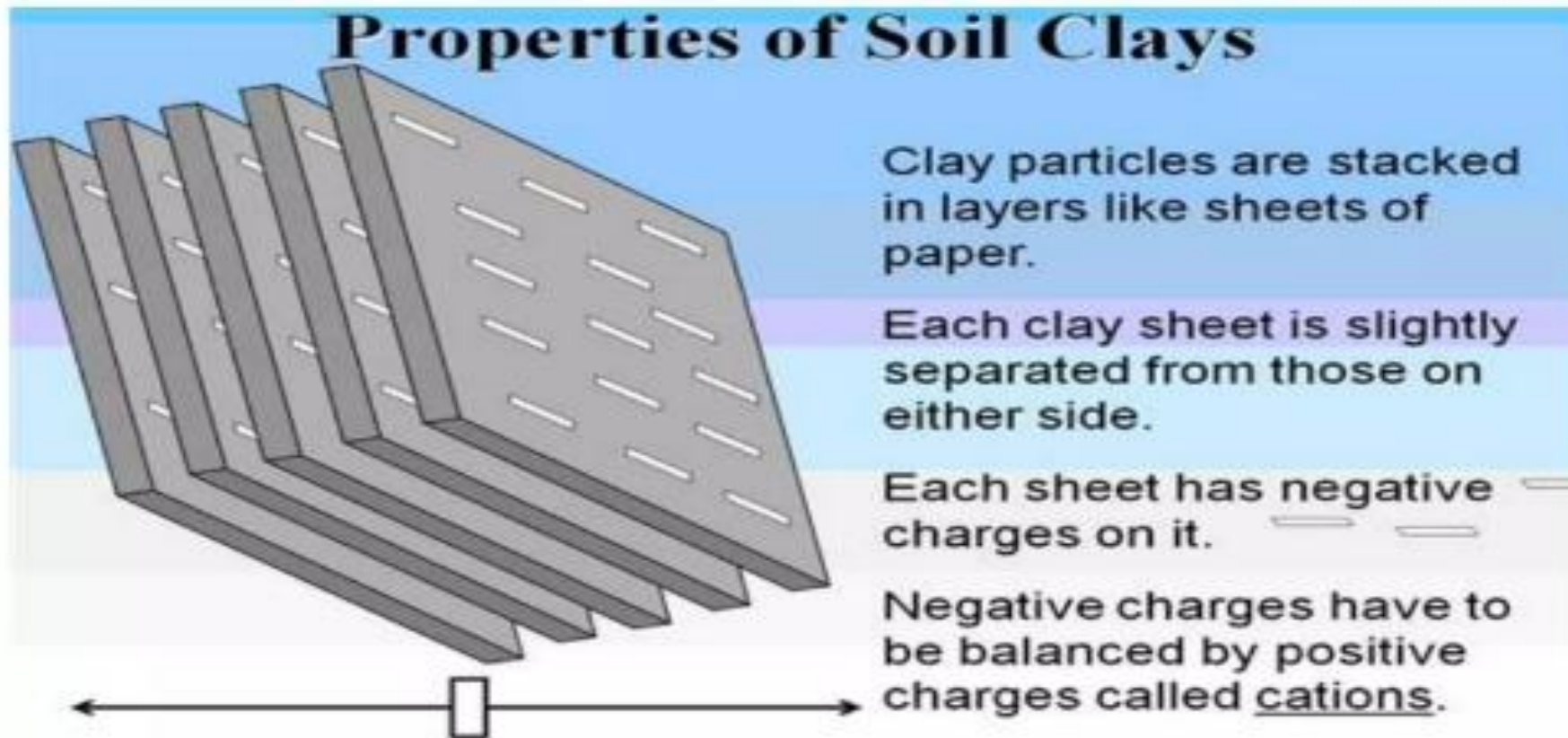
Ion exchange

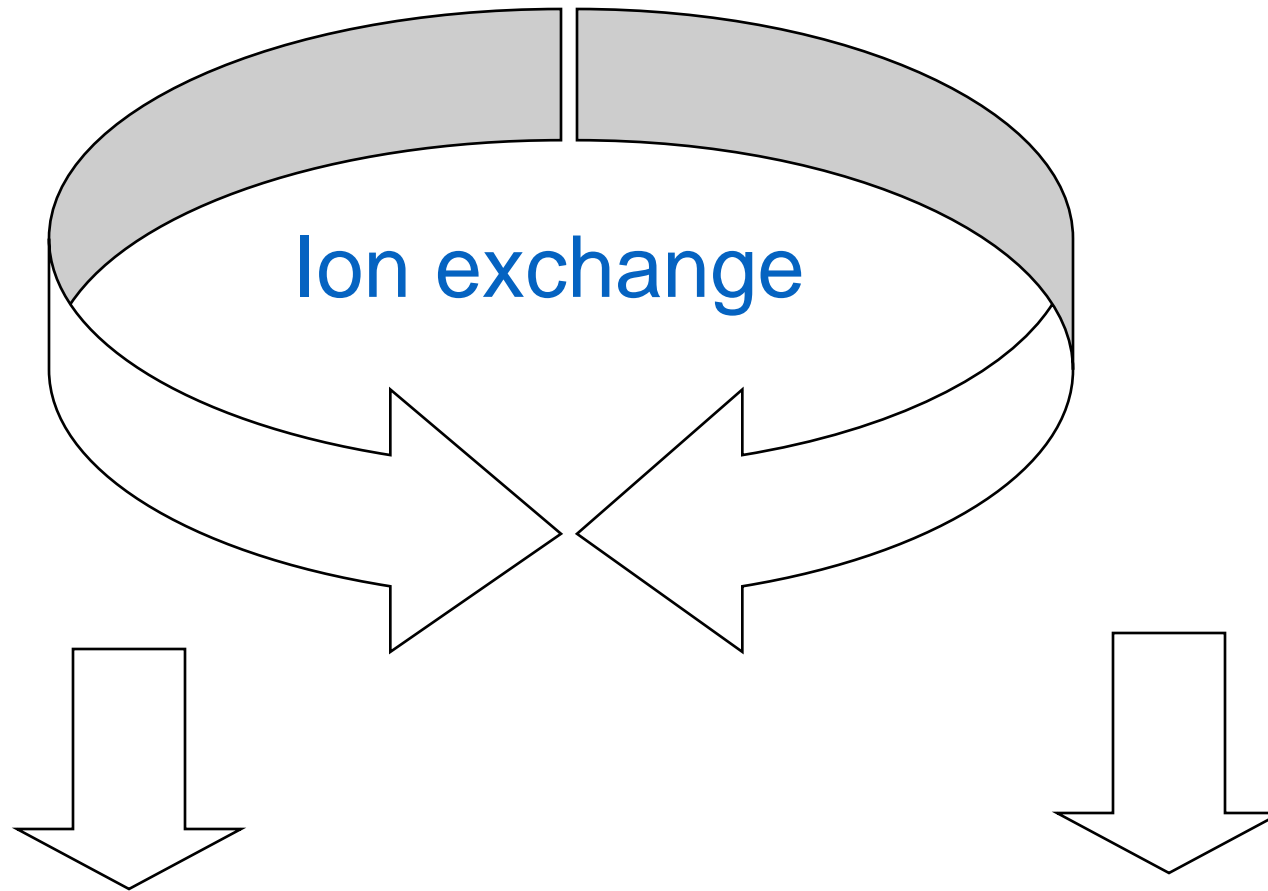
- Ion exchange is the exchange of ions between soil solution and colloidal complex
- Cations and anions in soil solution adsorbed by soil colloids such as silicate clays, hydrous oxides of Fe, Al and Humus



Ion exchange

- **Cation exchange**
- **Anion exchange**





Ion exchange

CEC

(CEC) cation exchange capacity:

The total amount of exchangeable cations that a particular material or soil can adsorb at a given pH

ACE

(AEC) anion exchange capacity:

The total amount of exchangeable anions that a particular material or soil can adsorb at a given pH

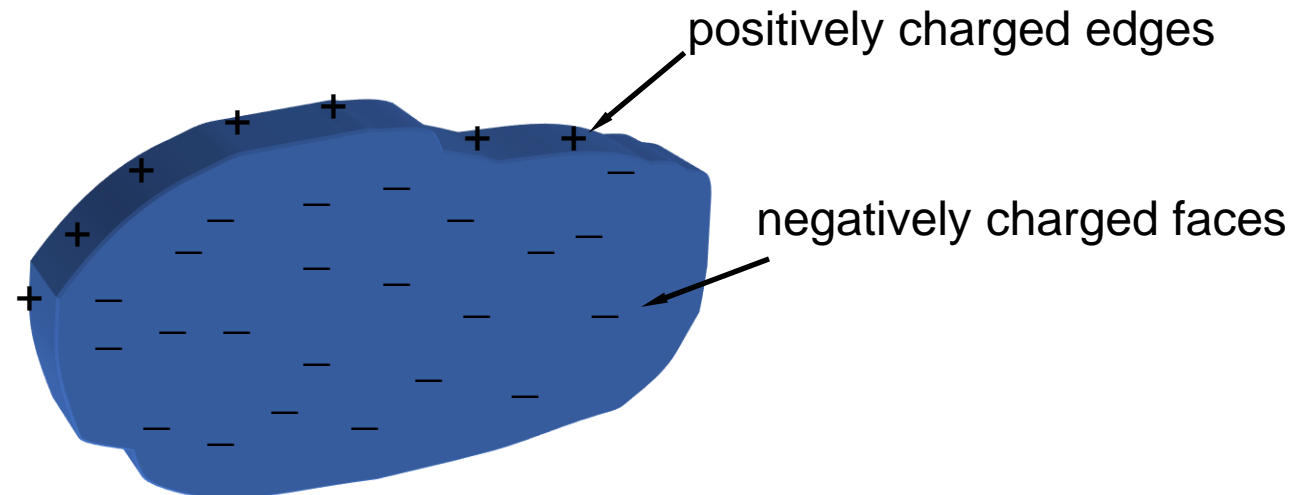
Sources of negative charges

- 1- Isomorphous substitution(%80 of negative charge).
- 2-Broken edges.
- 3- Broken bonds.
- 4- Crystal defects.

Isomorphous Substitution (pH-independent):

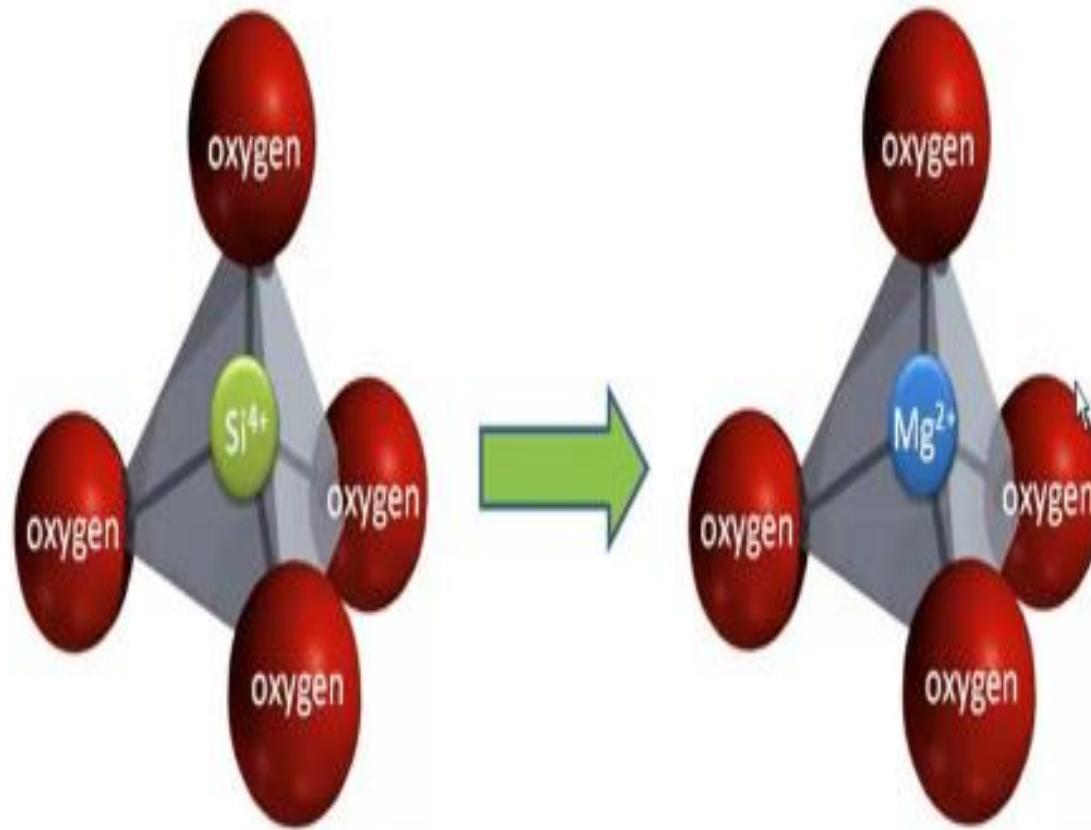
substitution of Si^{4+} and Al^{3+} by other lower valence (e.g., Mg^{2+}) cations it means lower charge cations replace higher charge cations .

results in charge imbalance (net negative)



Clay Particle with Net negative Charge

Mg²⁺ replace Si⁴⁺ in tetrahedron sheet, leaves net negative charge.



Net charge difference?

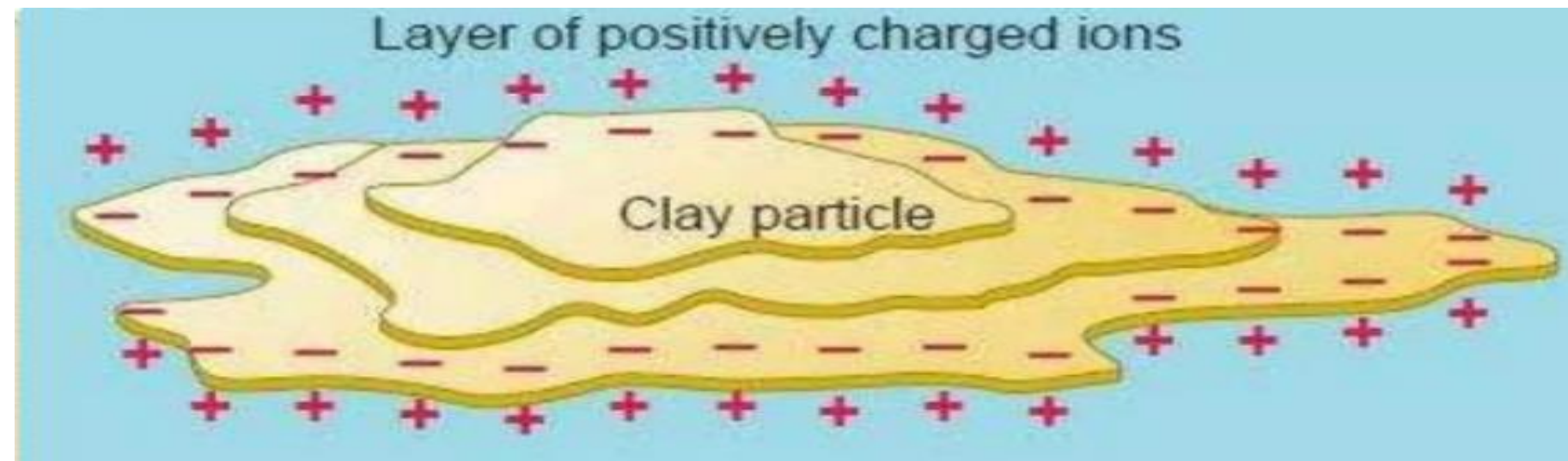
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pH independent (Isomorphous substitution)

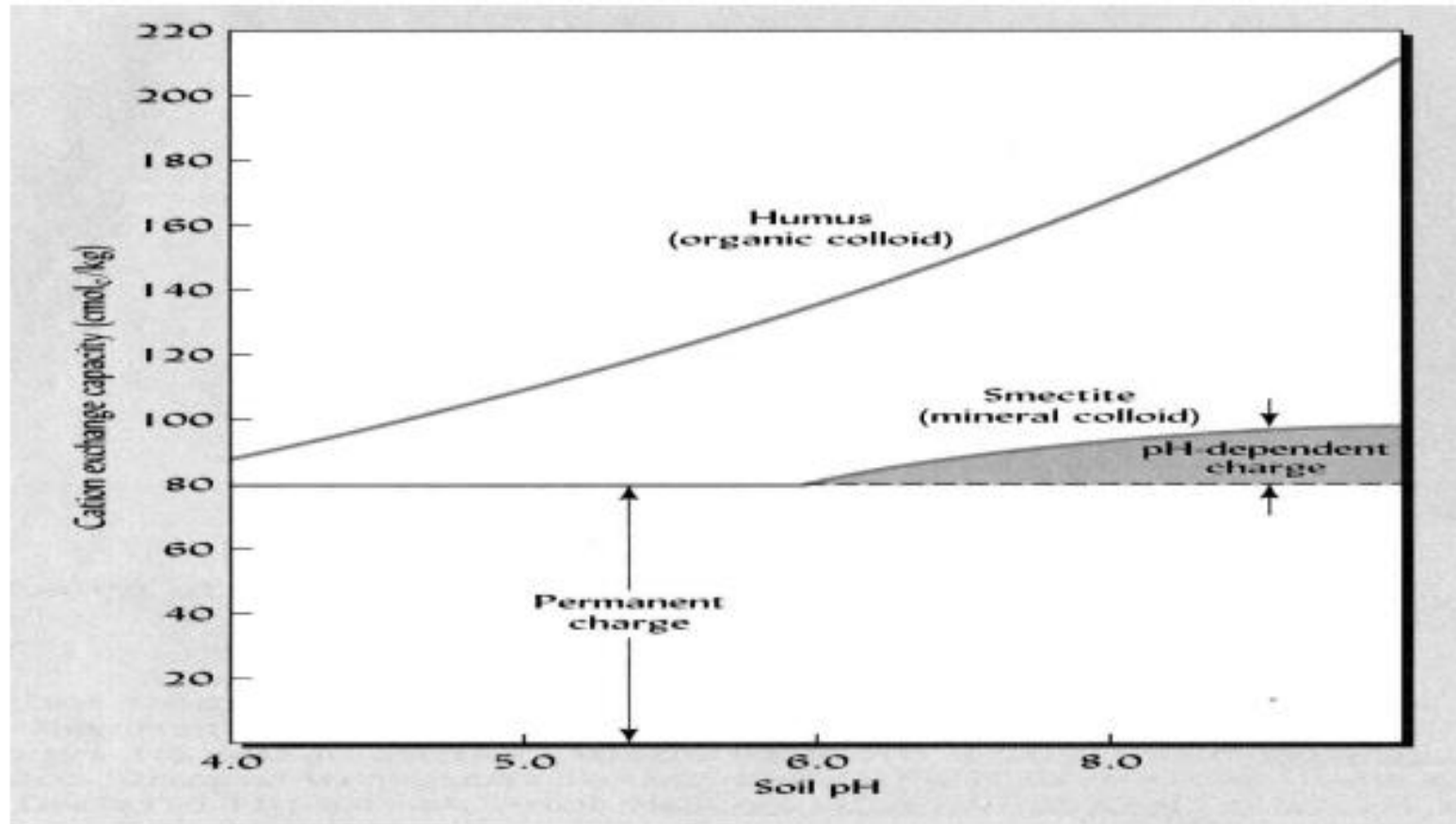
- Three positive charges of Al are satisfied with three negative charges of oxygen or hydroxyl - No net negative or positive charge
- When Mg^{2+} is replaced by Al^{3+} results an imbalance occurs
- Similar way negative charge develops due to isomorphous substitution
- Not dependent pH, referred to as permanent charges
- Substitution of one ion for the another ion of similar size but lower positive valence
- Si^{4+} replaced by Al^{3+} and even more extensive replacement of Al^{3+} by one or more of Fe^{3+} , Fe^{2+} , Mg^{2+} or Zn^{2+}
- Without substitution the positive and negative energy are in balance

pH dependent (Exposed crystal edges)

- Develops due to *unsatisfied valences at the broken edges of Si & Al sheets*
- Flat surface also serve as negative charges
- Oxygen and hydroxyl groups exposed at the broken edges
- $\text{pH} > 7.0$, the H ions of these OH group dissociates and negative charge carried by oxygen
- These type of charge develops in **1:1 clay minerals, organic colloids than other**



Effect of pH on negative charge in inorganic and organic colloids



Only 5-10% of the negative charge on 2:1 layer silicates is pH dependent whereas 50% or more of the charge developed on 1:1 minerals can be pH dependent.

pH independent charge (permanent)

Isomorphic substitution: substitution of one element for another in ionic crystals without changing the structure of the crystal

a. Substitution of Al^{+++} for Si^{++++} in tetrahedral

b. Mg^{++} , Fe^{++} , Fe^{+++} for Al^{+++} in octahedral

Leaves a net negative charge (permanent)

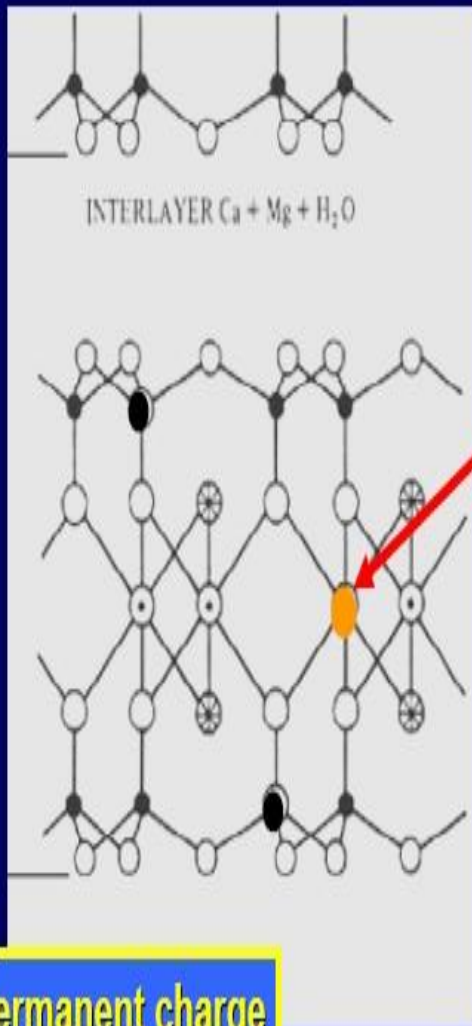
pH dependent charge: positive charge developed at low pH and excess negative charge formed at high pH. Gain or loss of H^+ from functional groups on the surface of soil solids.

a. Hydroxy ($-\text{OH}$)

b. Carboxyl ($-\text{COOH}$)

c. Phenolic ($-\text{C}_6\text{H}_4\text{OH}$)

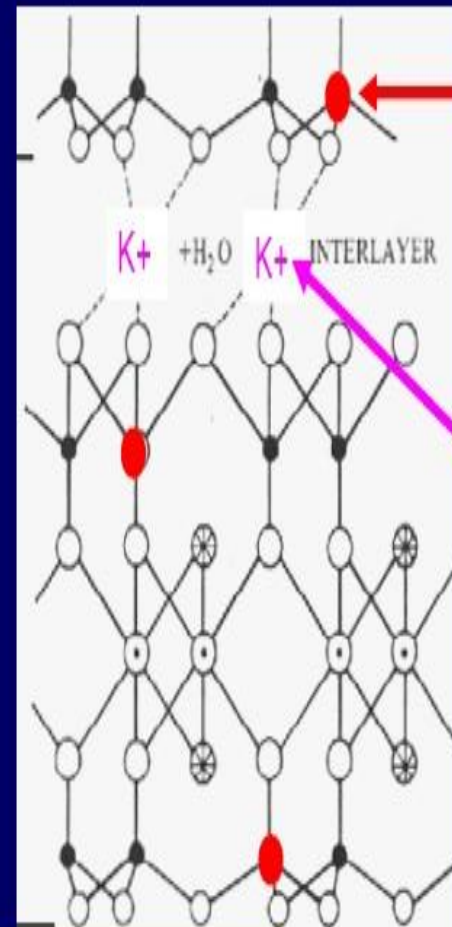
Source of charge for the smectites



Isomorphous substitution here, in the octahedral sheet means a net **NEGATIVE** charge

Permanent charge

Source of charge for the micas



1. Isomorphous substitution in **tetrahedral sheets**

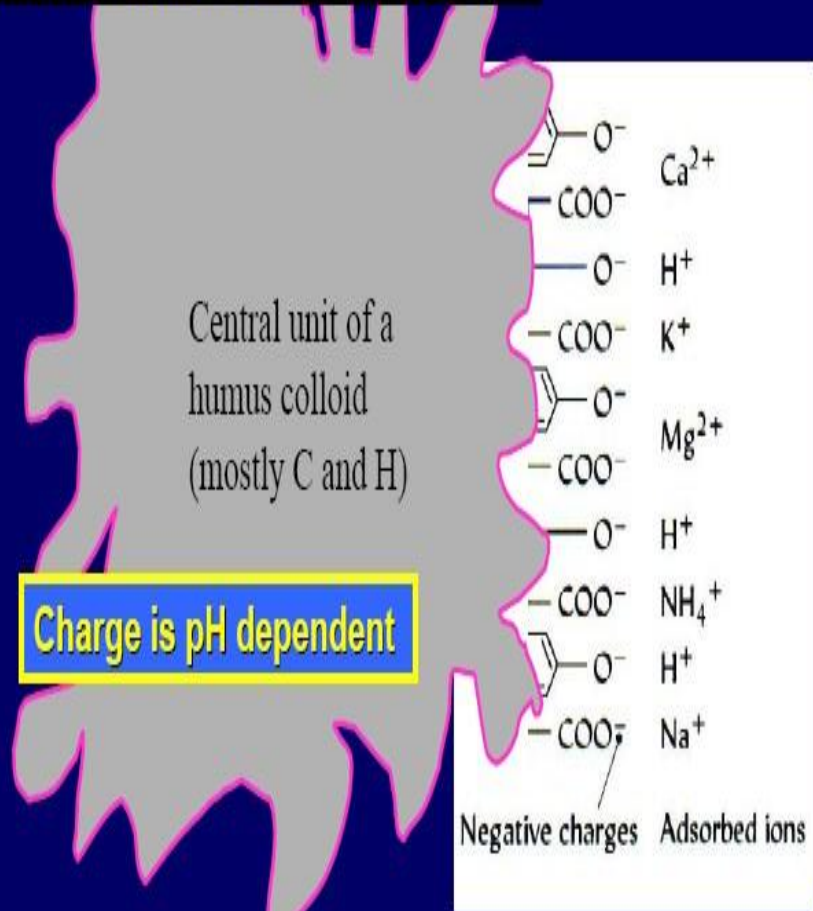
2. K⁺ satisfies charge and "locks up" the structure **no internal exchange surfaces**

3. Charge imbalance mostly on edges

Permanent charge

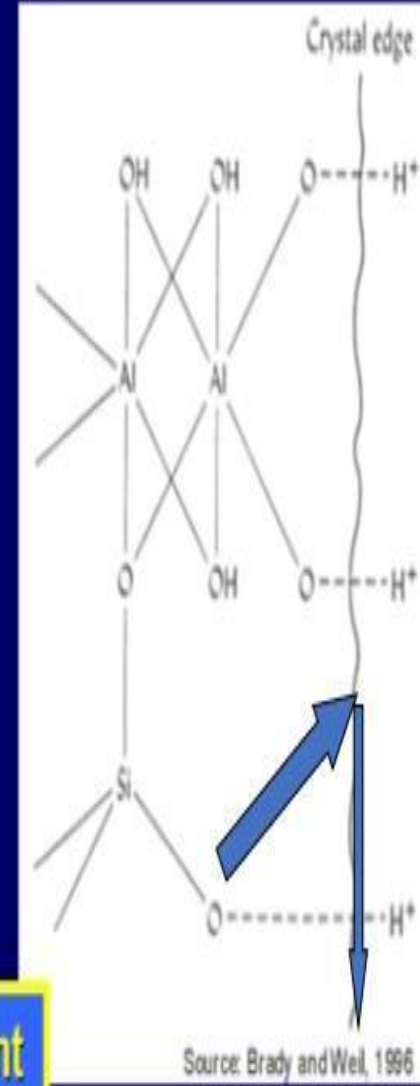
Negative charges on humus

ENORMOUS external surface area!
(but no internal surface – all edges)



Source of charge on 1:1 clays

Broken edge of a kaolinite crystal showing oxygen atoms as the source of **NEGATIVE** charge



Charge is pH dependent

Charges on soil colloids*

Colloid type	Negative charge	Positive charge
Humus (O.M.)	200 cmol _c /kg	10 cmol _c /kg
Silicate clays	100 cmol _c /kg	0 cmol _c /kg
Oxides of Al and Fe	4 cmol _c /kg	5 cmol _c /kg

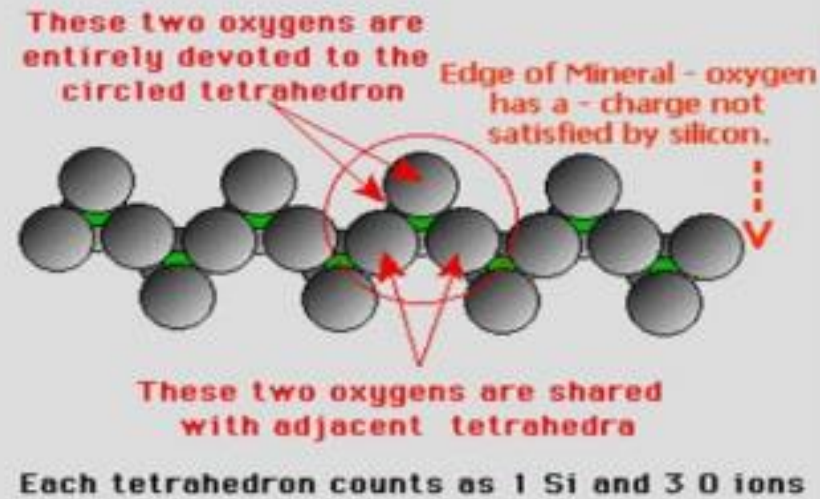
* Itty bitty soil components – silicate clays, oxides, humic substances

So what will those negative charges adsorb?

- Broken bonds at edge of clay mineral, broken edge of mineral showing oxygen atoms as the source of **negative** charge

Clay as a source of negative charge

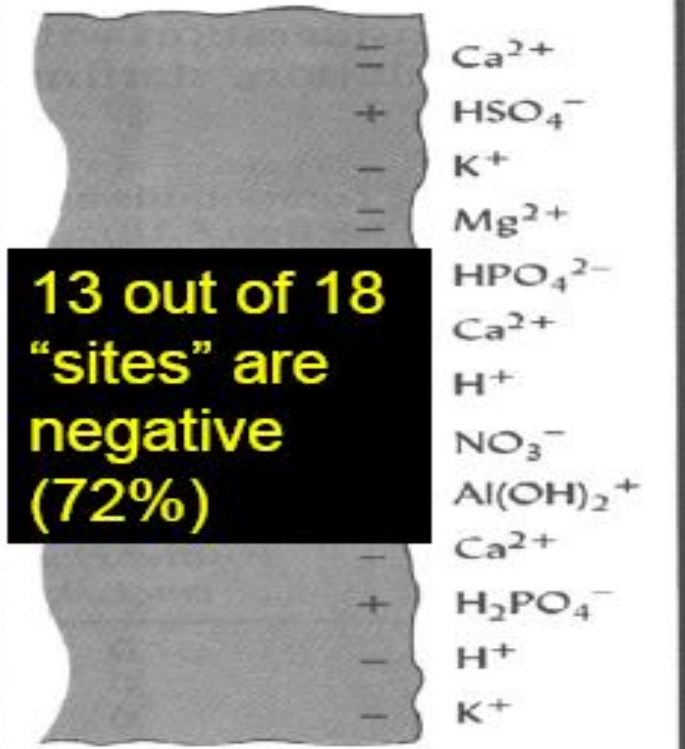
2. Source 1:
) broken bonds at edge of clay mineral



Positive charges

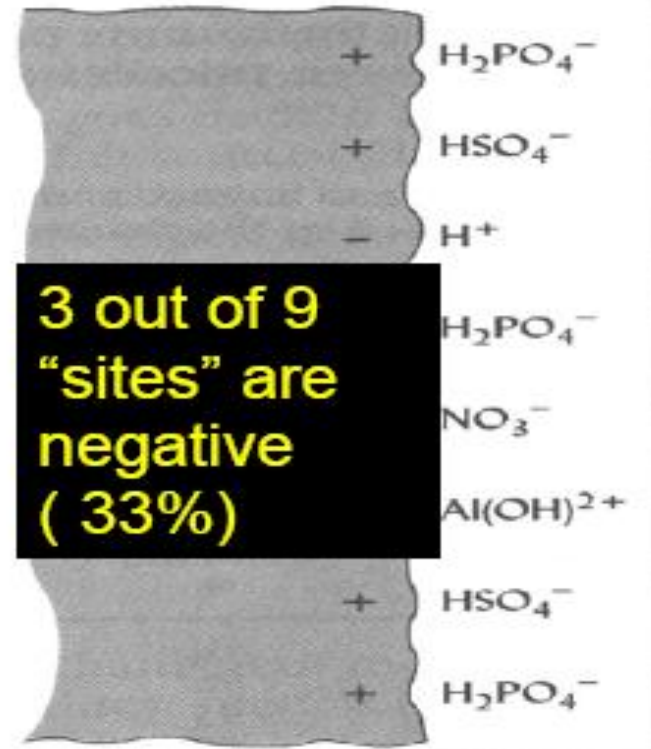
- Some soil colloids possess positive charges and attract anions
- Fe and Al oxides, clay minerals and amorphous clay minerals and layer silicates develop positive charges
- At soil pH is greater than ZPC (Zero Point Charge), the mineral is negative charge and absorbs cations
- At soil pH is lower than ZPC (Zero Point Charge), the mineral is positive charge and absorbs anions

Surface charge comparison



(a)

I:1-type silicate clay particle



(b)

Iron/aluminum oxide particle

Most soils have a net negative charge because of the negative charges in clay minerals and organic matter, but some highly weathered soils dominated by allophone and hydrous oxides may have a net positive charge at low pH.

The zero point charge (ZPC) has been used to characterize the relative abundance of positive and negative charges.

The zero point of charge is defined as the pH at which – and + charges are equal

Cation Exchange Capacity (CEC)

- The sum total of all **exchangeable cation charges** that a soil can adsorb
- Determined experimentally in the lab
- Expressed in terms of **positive charge adsorbed** per unit mass [$\text{cmol}_{\text{charge}}/\text{kg}_{\text{soil}}$]
- **If:** CEC = $10 \text{ cmol}_c/\text{kg}$
Then: soil adsorbs **10 cmol of H^+** which can be **exchanged** with **10 cmol K^+** , or **5 cmol Ca^{2+}**

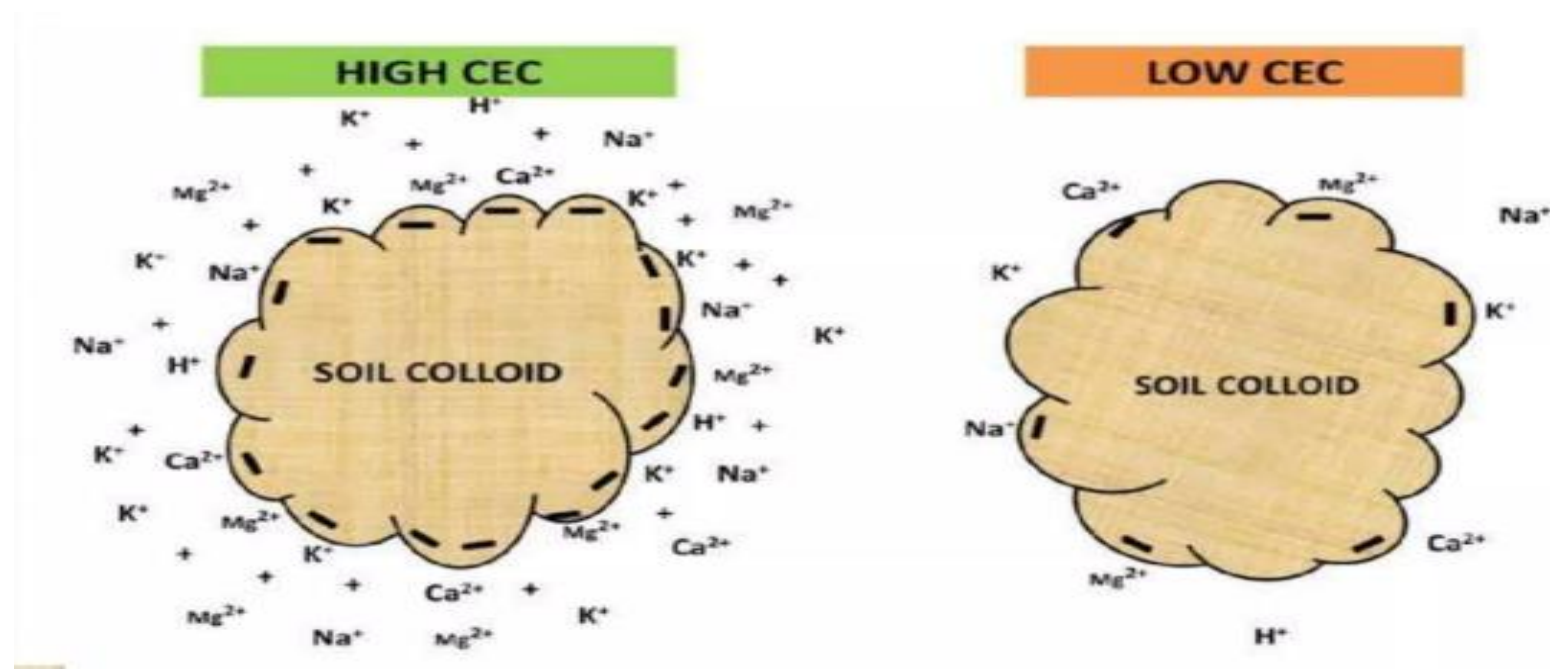
**Number of charges, not the number of ions,
is what matters**

Characteristic of cation exchange:-

- 1- Cation exchange reactions are **reversible processes**.
- 2- Cation exchange reactions are approximately **stoichiometric**, since the amount exchanged is chemically equivalent, one divalent cation exchanges with two monovalent cations.

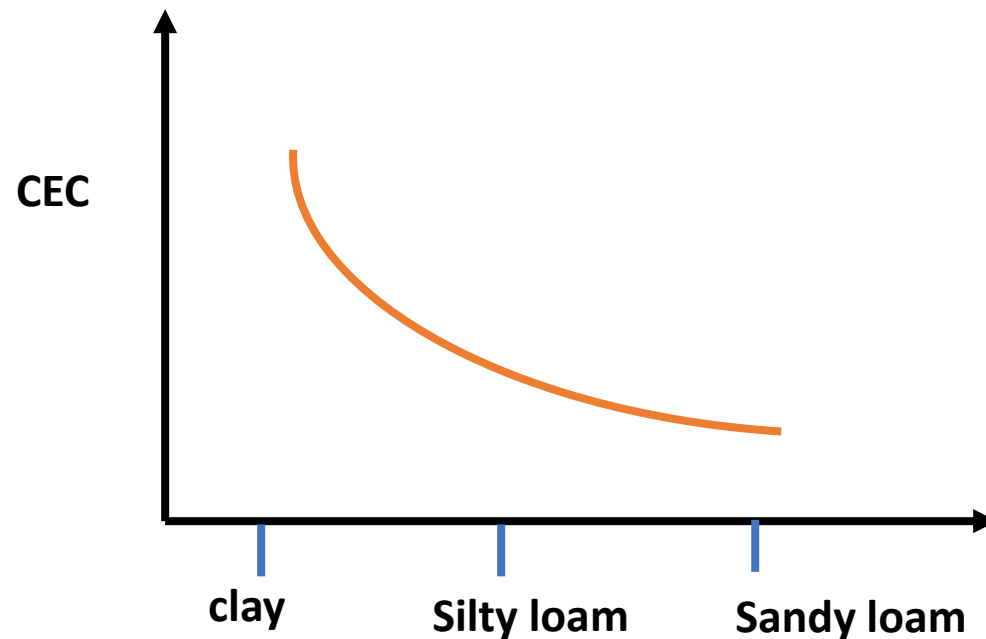


- 3- Cation exchange is controlled by mass action law



Factors affecting Cation Exchange Capacity:

1) Soil texture: The negatively charged clay colloids attract and hold positively charged cations. Therefore, the cation exchange capacity of soils increases with an increase in the percentage of clay content. **Clay soils with high CEC** can retain large amounts of cations and reduce the loss of cations by leaching. **Sandy soils, with low CEC**, retain smaller quantities of cations; therefore cations are removed from soil by leaching. (fine texture soil has more CEC than coarse soil texture)



2) clay minerals: The CEC of a soil dominated by smectite type of clay minerals is much higher than kaolinite type dominated soils. **soil with more amount of clay has higher CEC, 2:1(vermiculite - montmorillonite) type clay has more CEC than 1:1 type(kaolinite) of clay**

Cation exchange capacities of common clay minerals

Clay mineral		CEC (cmol _c /kg)
Kaolinite	low	3-15
Halloysite		5-50
Smectite	high	80-150
Illite		10-40
Vermiculite	really high	100-150
Chlorite		10-40

3) Soil Reaction(pH): The increase in the negative charge on the colloids (pH) caused , increase in CEC.

pH independent charge (permanent)

Isomorphic substitution: substitution of one element for another in ionic crystals without changing the structure of the crystal

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Leaves a net negative charge (permanent)

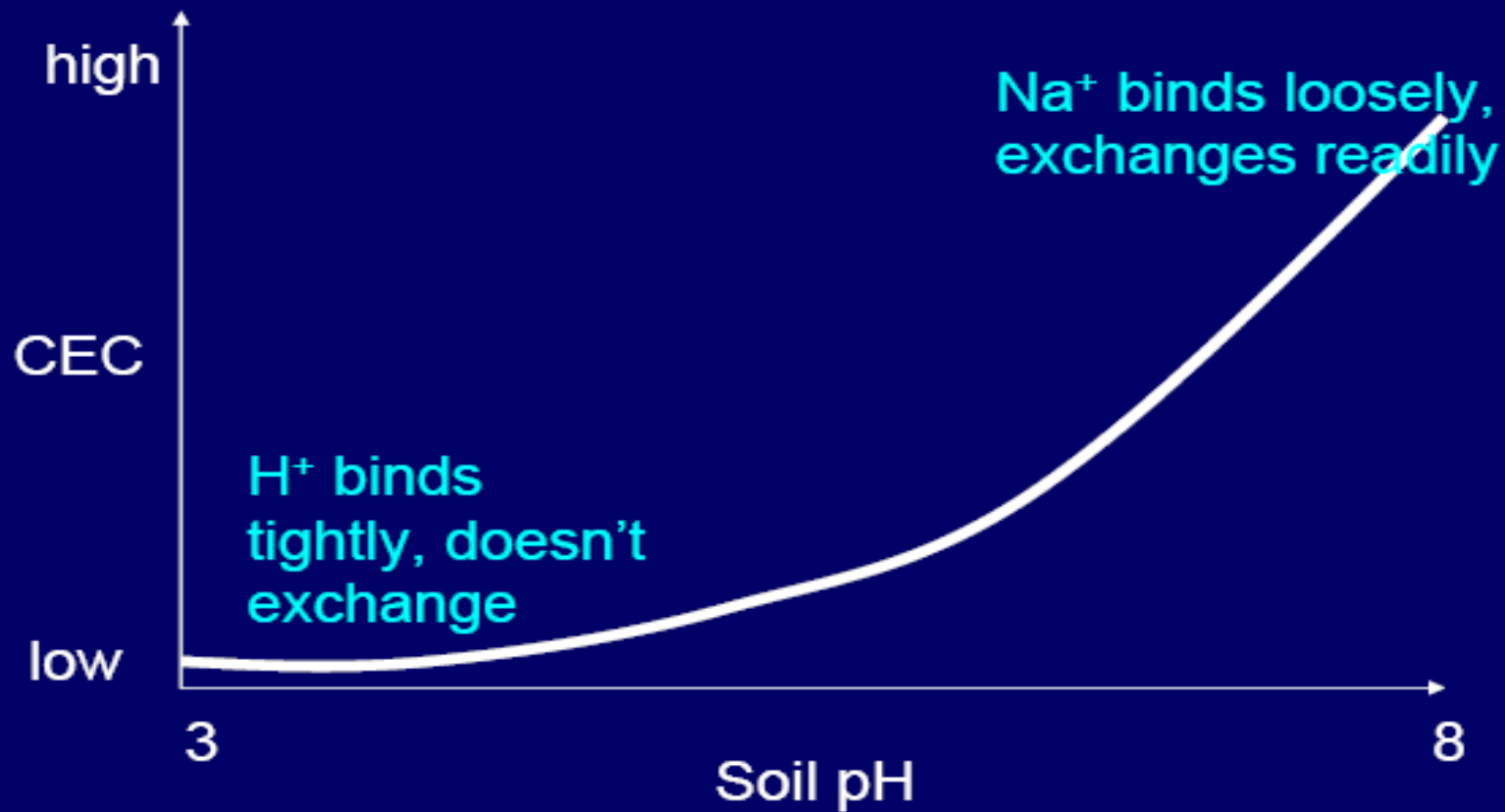
pH dependent charge: positive charge developed at low pH and excess negative charge formed at high pH. Gain or loss of H^+ from functional groups on the surface of soil solids.

a.Hydroxy (-OH)

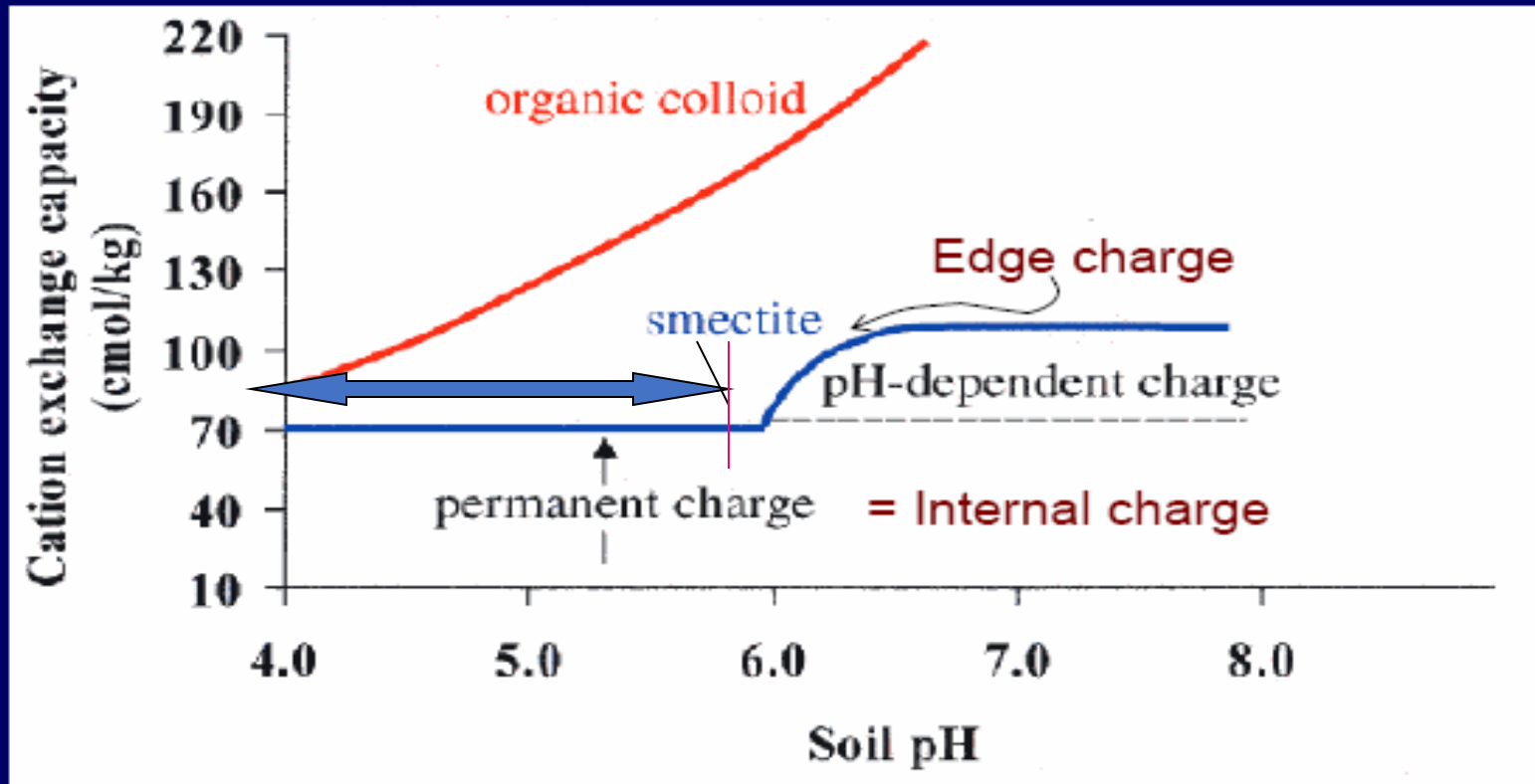
b.Carboxyl (-COOH)

c.Phenolic ($-C_6H_4OH$)

CEC and pH

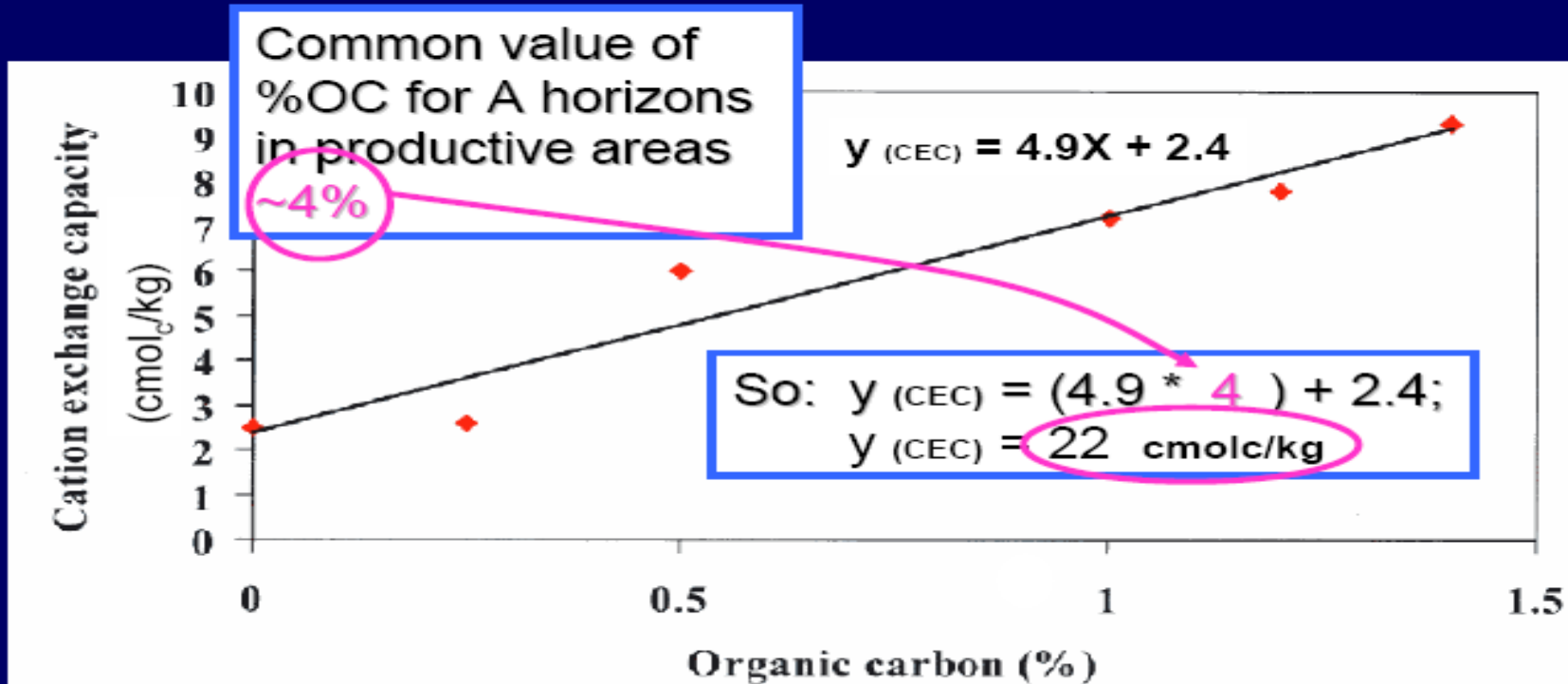


Influence of pH on the CEC of smectite and humus

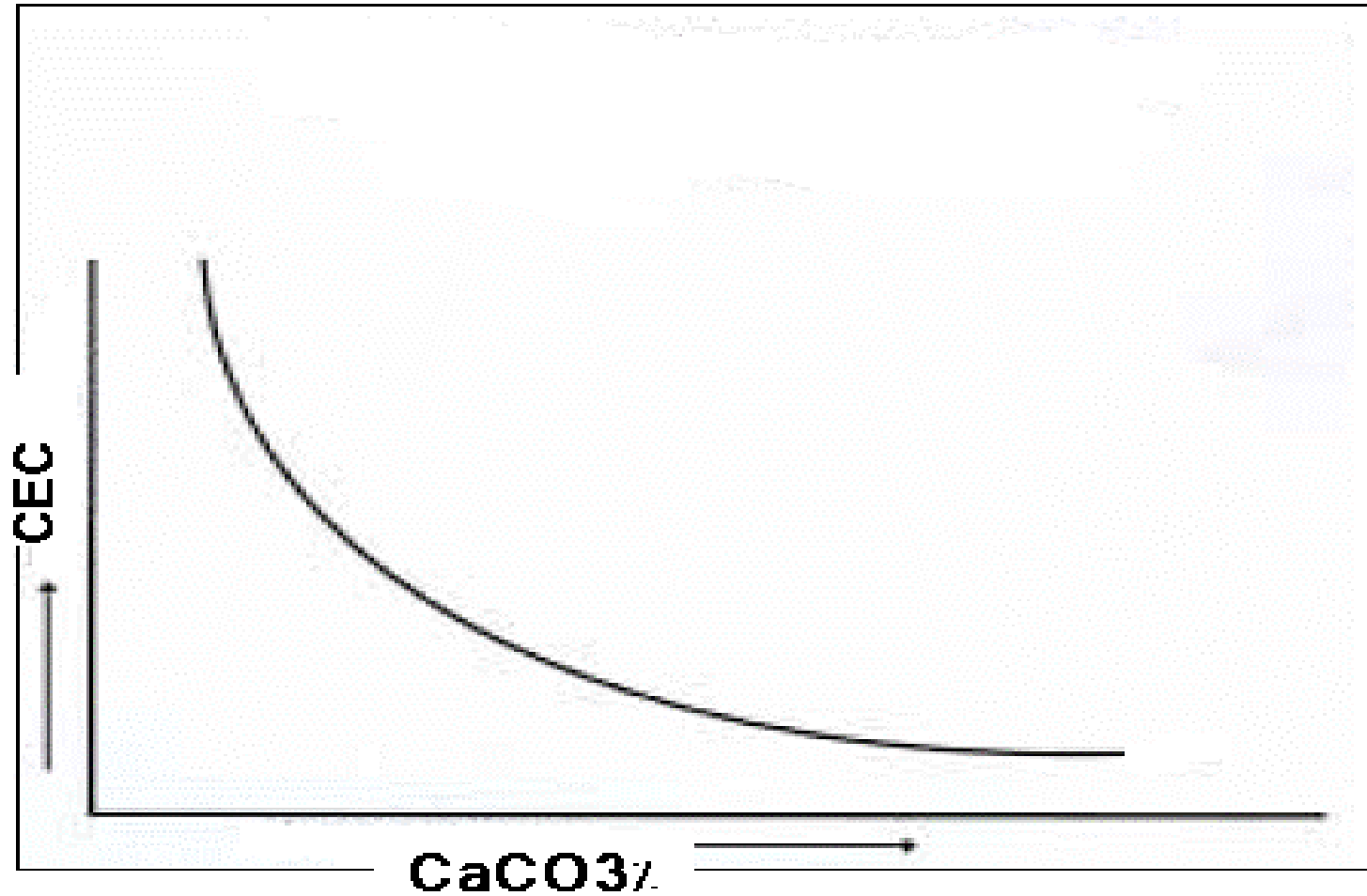


4) Soil organic matter: High organic matter content increases CEC. The CEC of clay minerals range from 10 to 150 [cmol /kg⁻¹] and that of organic matter ranges from 200 to 400 [cmol /kg⁻¹].

Organic matter and CEC



5) Effect of CaCO_3 on CEC: Increasing CaCO_3 content caused a decrease in CEC because CaCO_3 coats clay particles due to decreasing negative charge which decreases the CEC.



Importance of Cation Exchange

- Cation exchange is an important reaction in soil fertility, in causing and correcting soil acidity and basicity, in changes altering soil physical properties, and as a mechanism in purifying or altering percolating waters.
- The plant nutrients like calcium, magnesium, and potassium are supplied to plants in large measure from exchangeable forms.
- The amount of lime required to raise the pH of an acidic soil is greater as the CEC is greater.
- Cation exchange sites hold Ca^+ , Mg^+ , K^+ , Na^+ , and NH_4^+ ions and slow down their losses by leaching.
- Cation exchange sites hold fertilizer K^+ and NH_4^+ and greatly reduce their mobility in soils.
- Cation exchange sites adsorb many metals (Cd^{2+} , Zn^{2+} , Ni^{2+} , and Pb^{2+}) that might be present in wastewater adsorption remove them from the percolating water, thereby cleansing the water that drains into groundwater.

