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# **ASAC 1101 : FUNDAMENTALS OF SOIL SCIENCE (2+1)**

**Level : B.Sc (Ag), I semester**

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**SOIL SCIENCE AND AGRICULTURAL CHEMISTRY**

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## **Topic**

**Cation Exchange Capacity**

**Anion Exchange Capacity**

## Concepts Covered:

- What is CEC
- Methods of determining CEC
- CEC of different soils
- pH and CEC
- CEC in field soils
- Weathering and CEC/AEC

# Cation Exchange Capacity

- The CEC is expressed as the number of moles of positive charge adsorbed per unit mass.
- Units of CEC: Older unit- milliequivalents per 100 grams (me/100 g)

Another unit- centimoles of charge per kilogram (cmolc/kg)

- $1 \text{ me}/100 \text{ g} = 1 \text{ cmolc}/\text{kg}$
- CEC 15 cmolc/kg means – 1 kg soil can hold 15 cmol of positive ions.

# Methods of Determining CEC

## □ Buffer CEC Methods:

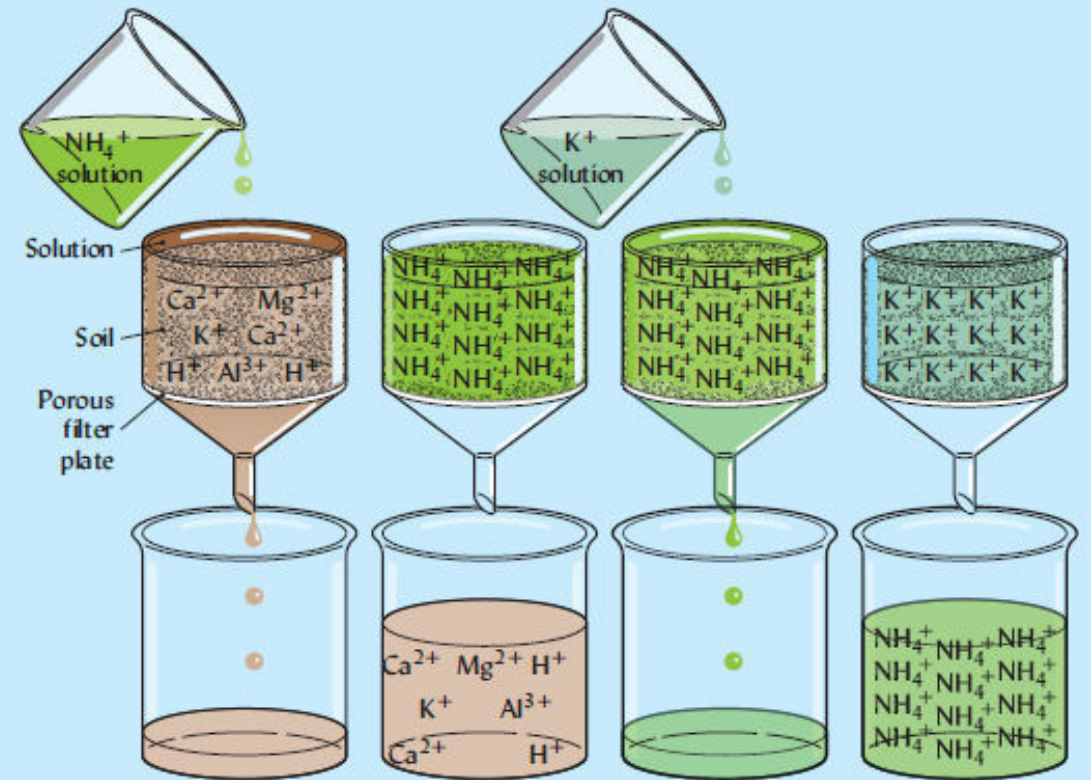
- The buffer solution is applied to the soil.
- If the pH of the buffer is more than the pH of the native soil then these methods measure not only the cation exchange sites active at the pH of the particular soil, but also any pH-dependent exchange sites that would become negatively charged if the soil pH were raised to pH 7.0 or 8.2.
- Thus these methods exaggerate the true CEC of acid soils.
- The buffered methods ( $\text{NH}_4^+$  at pH 7.0 or  $\text{Ba}^{2+}$  at pH 8.2) measure the potential or maximum cation exchange capacity of a soil.

**☐ Effective CEC (Unbuffered):**

- **The unbuffered method can measure only the effective CEC (ECEC) of the soils.**
- **This method gives a result when the pH of the native soil is lower than the buffer pH.**

# Steps for determining the CEC:

- The soil is leached with  $\text{NH}_4^+$  salt solution.
- $\text{NH}_4^+$  replaces the other cations.
- After removing excess of  $\text{NH}_4^+$  salt solution, soil is again leached with  $\text{K}^+$  salt solution.
- $\text{NH}_4^+$  washed into lower container. The concentration of the  $\text{NH}_4^+$  will be determined which the CEC of the soil.



# Calculating Soil CEC From Lab Data

- After leaching the soil with 0.4 L of  $\text{NH}_4^+$  solution, all the exchangeable cations shown in the soil sample were displaced off the colloids and washed into the beaker along with the excess  $\text{NH}_4^+$  ions. The solution in this beaker (*b*) was analyzed for Ca, Mg, K, Al, and H with the following results: 200 mg/L  $\text{Ca}^{2+}$ , 60 mg/L  $\text{Mg}^{2+}$ , 97.5 mg/L  $\text{K}^+$ , 5 mg/L  $\text{H}^+$ , and 67.5 mg/L  $\text{Al}^{3+}$ . Because only 0.4 L of solution was collected from the soil sample and the soil sample weighed only 0.1 kg, these results can be multiplied by 0.4 and 10 to give the amounts of each ion collected in mg/kg soil. As an example we can show the calculation for  $\text{Ca}^{2+}$  as:

$$\frac{200 \text{ mg Ca}^{2+}}{\text{L}} \times \frac{0.4 \text{ L}}{\text{sample}} \times \frac{10 \text{ samples}}{\text{kg soil}} = \frac{800 \text{ mg Ca}^{2+}}{\text{kg soil}}$$

- For  $\text{Ca}^{2+}$  the atomic weight is approximately 40 g/mol, so we calculate the cmol of exchangeable  $\text{Ca}^{2+}$  in 1 kg soil:

$$\frac{800 \text{ mg Ca}^{2+}}{\text{kg soil}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Ca}^{2+}}{40 \text{ g}} \times \frac{100 \text{ cmol}}{\text{mol}} = \frac{2 \text{ cmol Ca}^{2+}}{\text{kg soil}}$$



- Repeating this calculation for each element provides the following results: 2 cmol Ca<sup>2+</sup>/kg, 1 cmol Mg<sup>2+</sup>/kg, 1 cmol K<sup>+</sup>/kg, 2 cmol H<sup>+</sup>/kg, and 1 cmol Al<sup>3+</sup>/kg. We now must multiply the cmol/kg for each element by the valence of the ion to convert to the cmol of *charge* (cmol<sub>c</sub>/kg) from that element. Using Ca<sup>2+</sup> again as an example:

$$\frac{2 \text{ cmol Ca}^{2+}}{\text{kg soil}} \times \frac{2 \text{ cmol}_c \text{ from Ca}^{2+}}{\text{cmol Ca}^{2+}} = \frac{4 \text{ cmol}_c \text{ from Ca}^{2+}}{\text{kg soil}}$$

- Repeating this calculation provides the following results: 4 cmolc Ca<sup>2+</sup>/kg, 2 cmolc Mg<sup>2+</sup>/kg, 1 cmolc K<sup>+</sup>/kg, 2 cmolc H<sup>+</sup>/kg, and 3 cmolc Al<sup>3+</sup>/kg. Assuming the five elements measured account for nearly all the exchangeable cations, the sum of their charges (4 + 2 + 1 + 2 + 3 = 12) equals the CEC of our soil: **12 cmolc/kg**.

## 2<sup>nd</sup> method

- Measure the amount of  $\text{NH}_4^+$  .
- Assume the  $\text{NH}_4^+$  concentration in beaker *d* to be 540 mg  $\text{NH}_4^+$ /L. As in method 1, because only 0.4 L of solution was collected from the soil sample and the soil sample weighed only 0.1 kg, these results can be calculated as follows to give the amount of  $\text{NH}_4^+$  ions collected in mg/kg soil:

$$\frac{540 \text{ mg NH}_4^+}{\text{L}} \times \frac{0.4 \text{ L}}{\text{sample}} \times \frac{10 \text{ samples}}{\text{kg soil}} = \frac{2160 \text{ mg NH}_4^+}{\text{kg soil}}$$

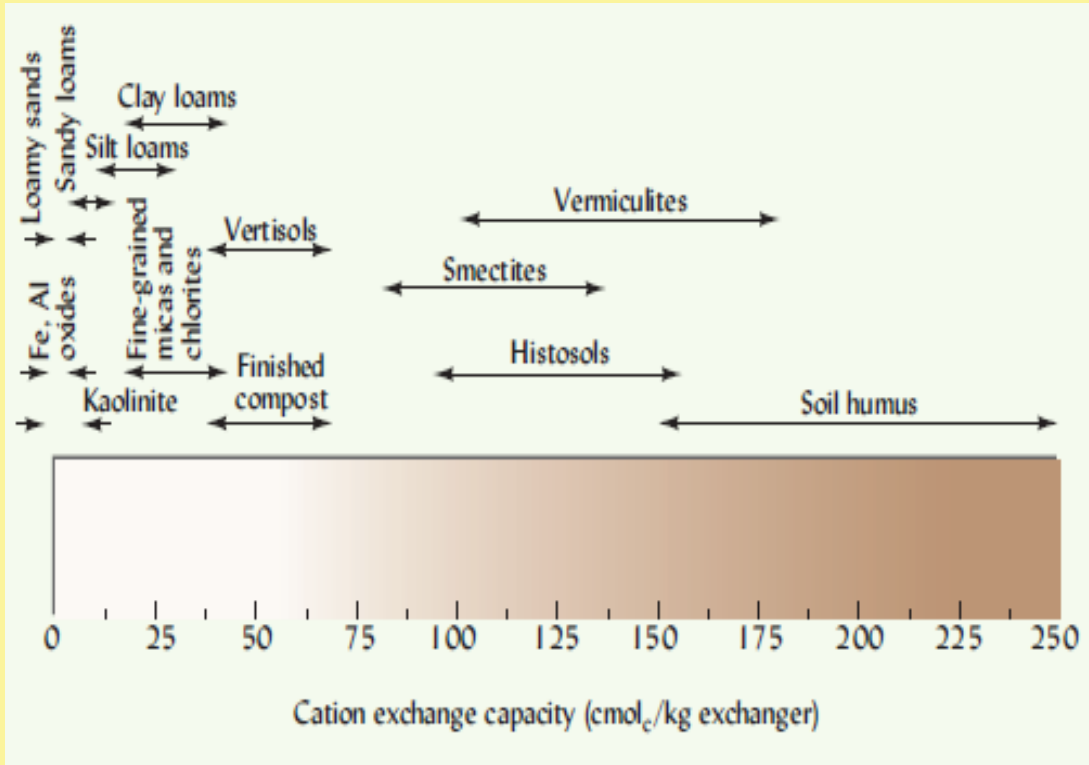
- Now convert it to cmolc/kg

$$\frac{2160 \text{ mg NH}_4^+}{\text{kg soil}} \times \frac{1 \text{ mol NH}_4^+}{10 \text{ g}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{100 \text{ cmol}}{\text{mol}} \\ = \frac{12 \text{ cmol NH}_4^+}{\text{kg soil}}$$

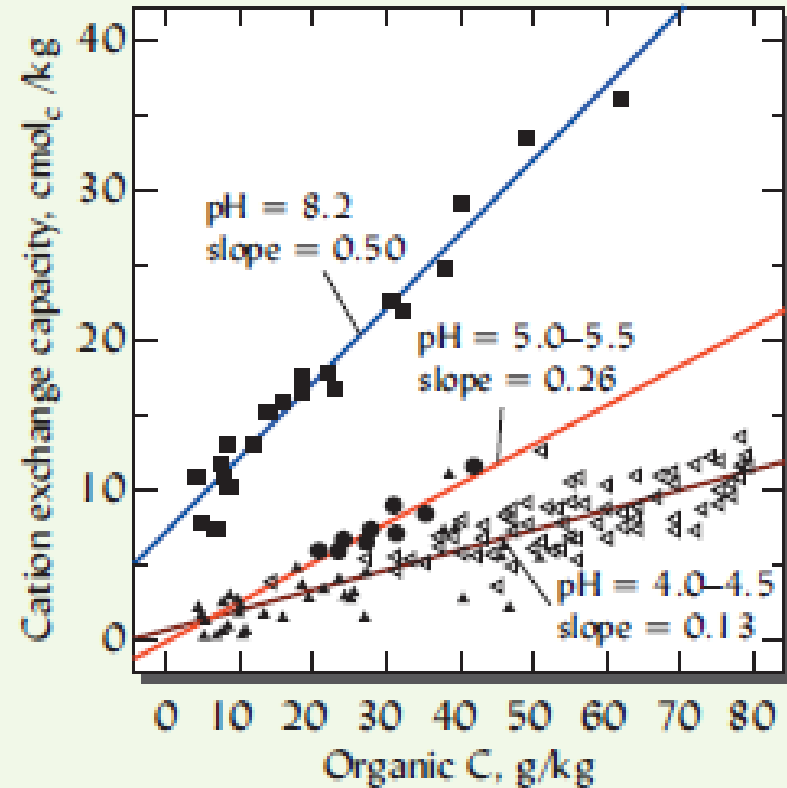
- The answer is **12 cmolc/kg**.

# CEC of different soils

- Sandy soils are low in CEC but clay soils are having high CEC values.
- Fe and Al oxides, Kaolinite are having low CEC (<10 cmol<sub>c</sub>/kg)
- Mica and chlorites = 10-40 cmol<sub>c</sub>/kg.
- Smectite and vermiculites ranges from 80-180 cmol<sub>c</sub>/kg.
- Humus is having the highest CEC (>250 cmol<sub>c</sub>/kg).



- At higher pH, soil humus contributes more CEC to the soil with a constant amount of clay.
- At pH 4-4.5, 1g of soil humus increases the CEC 0.13cmolc/kg.
- At pH 5-5.5, it increases the CEC 0.26cmolc/kg. Double than the earlier.



# Common ranges of potential CEC

| Soil order | Common range of CEC, <sup>a</sup> cmol <sub>e</sub> /kg | Soil order             | Common range of CEC, cmol <sub>e</sub> /kg |
|------------|---|------------------------|--|
| Histosols  | 110-170   | Inceptisols & Entisols | 5-37                                       |
| Vertisols  | 33-67   | Aridisols              | 7-29                                       |
| Andisols   | 13-49   | Alfisols               | 4-26                                       |
| Spodosols  | 2-57  | Ultisols               | 3-15                                       |
| Mollisols  | 12-36   | Oxisols                | 2-13                                       |

# Estimating CEC and clay mineralogy

## 1. Estimating CEC from Mineralogy

The dominant clays in Mollisols are likely 2:1 types such as vermiculite and smectite. Thus, the average CEC of the clays of these types to be about 100 cmolc/kg clay. At pH 7.0 the CEC of OM is about 200 cmolc/kg. Since 1 kg of this soil has 0.20 kg (20%) of clay and 0.04 kg (4%) of OM, we can calculate the CEC associated with each of these sources.

- From the clays in this Mollisol:  $0.2 \text{ kg} * 100 \text{ cmolc/kg} = 20 \text{ cmolc}$
- From the OM in this Mollisol:  $0.04 \text{ kg} * 200 \text{ cmolc/kg} = 8 \text{ cmolc}$
- The total CEC of this Mollisol:  $20 + 8 = 28 \text{ cmolc/kg soil}$



## 2. Estimating Clay Mineralogy from CEC

- Assume you know that a soil contains 60% clay and 4% Organic matter and the pH = 4.2. You also know the CEC is 5.8 cmolc/kg. You want to estimate the types of clays present. At pH 4.2 the CEC of the organic matter would be comparatively low, about 100 cmolc/kg.
- Therefore we estimate: CEC from OM in 1 kg soil = 0.04 kg OM \* 100 cmolc /kg OM = 4.0 cmolc
- The remaining portion of the CEC contributed by the clay can be estimated as:  
CEC from the clay in 1 kg soil = 5.8 cmolc - 4.0 cmolc = 1.8 cmolc
- Since this 1.8 cmolc/kg soil is provided by 0.60 kg of clay (60% of 1 kg soil), we can estimate:  
CEC of the pure clay = 1.8 cmolc/kg soil \* 1 kg soil/0.60 kg clay = 3 cmolc/kg clay
- From the previous table we can identify the soil and soil order by their respective CEC.

# pH and CEC

- **Generally CEC increases with pH.**
- **The permanent charge of 2:1, pH depended charge of humus and allophane and some 1:1 clay hold exchangeable ions.**
- **As the pH is raised, the negative charges on some 1:1-type silicate clays, allophane, humus, and even Fe, Al oxides increases and CEC also increases.**
- **In alkaline condition CEC reflects the pH depended charge as well as the permanent ones.**
- **So, the determination of CEC is generally done at pH 7 or 8.2.**

# Exchangeable cations in field soils

- The exchangeable ions in the soils depend upon the climatic condition.
- $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , complex aluminum hydroxy ions, and  $\text{H}^+$  are most prominent in humid regions.
- $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  dominate soil in low-rainfall areas.
- In a given soil, the proportion of the cation exchange capacity satisfied by a particular cation is termed the saturation percentage for that cation.
- If, 50% of the CEC is satisfied by  $\text{Ca}^{2+}$  ions, the exchange complex is said to have a *calcium saturation percentage* of 50.
- This terminology is especially useful in identifying the relative proportions of sources of acidity and alkalinity in the soil solution

## Cation Exchange Properties Typical for Unamended Clay Loam Surface Soils in Different Climatic Regions

| Property  | Warm, humid region (Ultisols) <sup>a</sup> | Cool, humid region (Alfisols) | Semiarid region (Ustolls) | Arid region (Natragids) <sup>b</sup> |
|---|--|-------------------------------|---------------------------|--------------------------------------|
| Exchangeable H <sup>+</sup> and Al <sup>3+</sup> , cmol <sub>e</sub> /kg (% of CEC) | 7.5 (75%)                                  | 5 (28%)                       | 0 (0%)                    | 0 (0%)                               |
| Exchangeable Ca <sup>2+</sup> , cmol <sub>e</sub> /kg (% of CEC)                    | 2.0 (20%)                                  | 9 (50%)                       | 17 (65%)                  | 13 (50%)                             |
| Exchangeable Mg <sup>2+</sup> , cmol <sub>e</sub> /kg (% of CEC)                    | 0.4 (4%)                                   | 3 (17%)                       | 6 (23%)                   | 5 (19%)                              |
| Exchangeable K <sup>+</sup> , cmol <sub>e</sub> /kg (% of CEC)                      | 0.1 (1%)                                   | 1 (5%)                        | 2 (8%)                    | 3 (12%)                              |
| Exchangeable Na <sup>+</sup> , cmol <sub>e</sub> /kg (% of CEC)                     | Tr   | 0.02 (0.1%)                   | 1 (4%)                    | 5 (19%)                              |
| CEC, <sup>c</sup> cmol <sub>e</sub> /kg   | 10   | 18                            | 26                        | 26                                   |
| Probable pH   | 4.5–5.0                                    | 5.0–5.5                       | 7.0–8.0                   | 8–10                                 |
| Nonacid cations (% of CEC) <sup>d</sup>   | 25%  | 68%                           | 100%                      | 100%                                 |

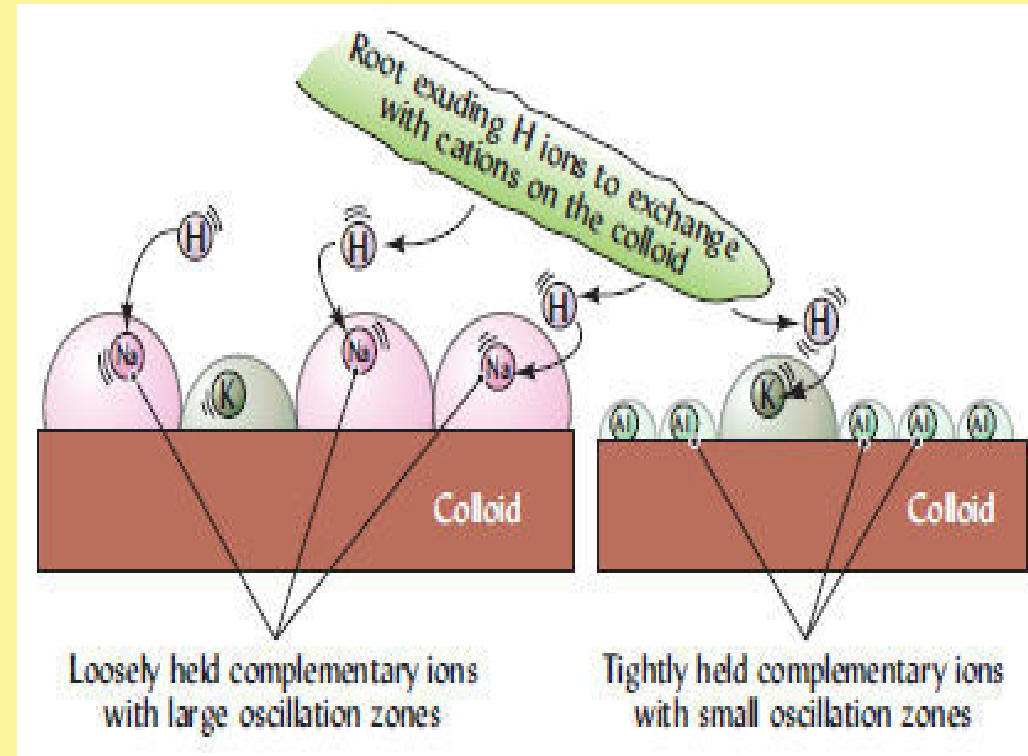
## Cation Saturation and Nutrient Availability

- If, the percent saturation of some ions are high then those ions will be easily and rapidly displaceable.

## Influence of Complementary Cations

- The strength of adsorption of common cations on most colloids is in the order:  
 $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ = \text{NH}_4^+ > \text{Na}^+$
- So,  $\text{K}^+$  can be easily replaced by  $\text{Al}^{3+}$  ions in the acid soil and it will be available for the plants.
- There are also some nutrient antagonisms that in certain soils cause inhibition of uptake of some cations by plants.
- Sometimes, high potassium levels are known to limit the uptake of magnesium even when significant quantities of magnesium are present in the soil.

- The half circles are loosely held with soil.
- The root will take cations from the soil in exchange of  $H^+$ .
- In the left figure, the loosely held  $Na^+$  will be easily taken up by the plant.
- In the right figure, the  $K^+$  will be easily taken up by the plant.
- The  $K^+$  will be comparatively more vulnerable to be replaced and sent to the soil solution.
- $K^+$  will be more available for plant uptake and leaching.

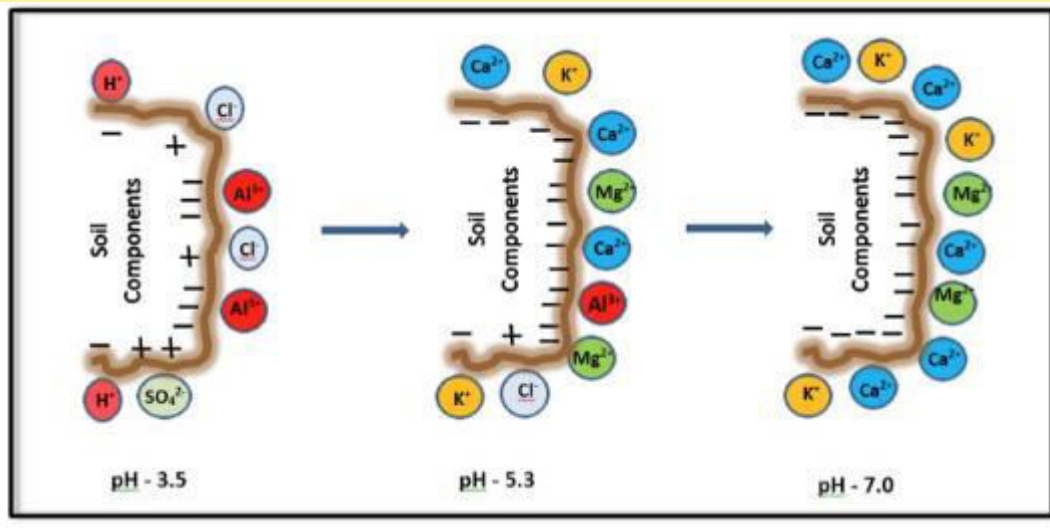


# Percent base saturation (BS)

- % of the CEC occupied by the basic cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^{+}$ . Basic cations are distinguished from the acid cations  $\text{H}^{+}$  and  $\text{Al}^{3+}$ . At an approximate soil pH 5.4 or less,  $\text{Al}^{3+}$  is present in a significantly high concentration that hinders growth of most plant species, and the lower the soil pH, the greater the amount of toxic  $\text{Al}^{3+}$ . Therefore, soils with a high percent base saturation are generally more fertile because:
- They have little or no acid cation  $\text{Al}^{3+}$  that is toxic to plant growth.
- Soils with high percent base saturation have a higher pH; therefore, they are more buffered against acid cations from plant roots and soil processes that acidify the soil (nitrification, acid rain, etc.).
- They contain greater amounts of the essential plant nutrient cations  $\text{K}^{+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  for use by plants.

# Percent base saturation (BS)

- $\%BS = [(Ca^{2+} + Mg^{2+} + K^+)/CEC] \times 100$



Depending on soil pH, the soil's base saturation may be a fraction of CEC or approximately equal to CEC. In general, if the soil pH is below 7, the base saturation is less than CEC. At pH 7 or higher, soil clay mineral and organic matter surfaces are occupied by basic cations, and thus, base saturation is equal to CEC.



# Effect of colloid types

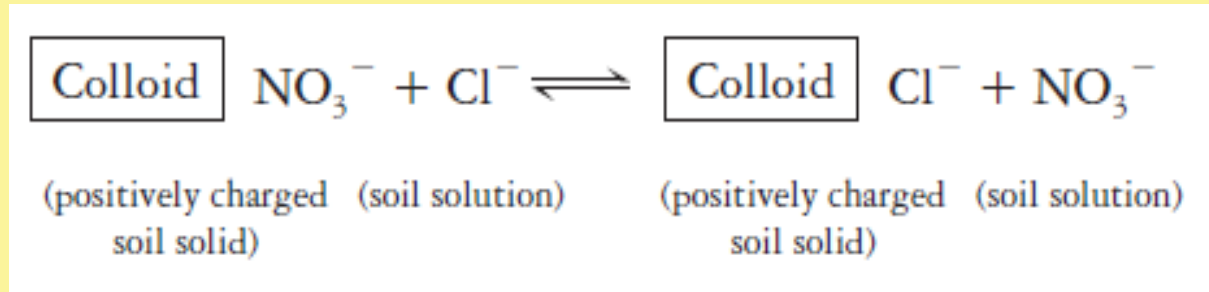
- Differences exist in the tenacity with which several types of colloids hold specific cations.
- At a given percentage base saturation, smectites which have a high charge density per unit of colloid surface hold calcium much more strongly than does kaolinite.
- So, Ca % will have to be increased upto a certain % to satisfy the need of plants in case of smectites.
- Kaolinite can supply Ca at relatively lower % of base saturation.
- The need to add limestone to the two soils will be somewhat different, partly because of this factor.

# Anion exchange

- Anions are held in two major ways.
- Firstly, they are held by anion adsorption mechanisms similar to those responsible for cation exchange.
- Secondly, they may actually react with surface oxides or hydroxides, forming more definitive inner-sphere complexes.

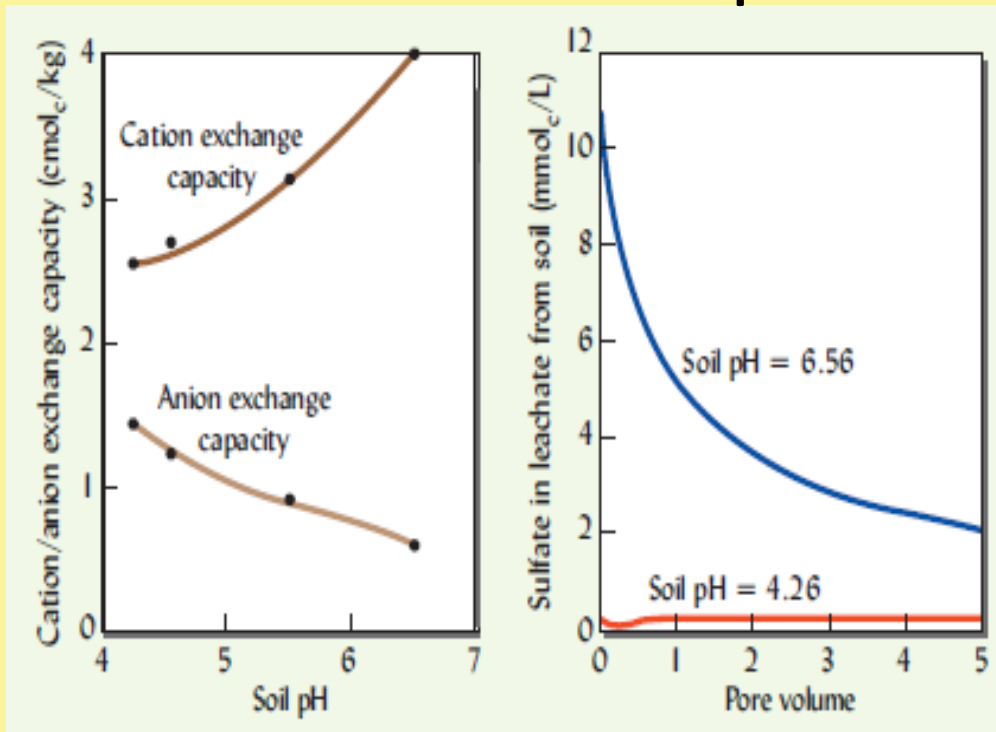
## Anion adsorption mechanisms

- The basic principles of anion exchange are similar to those of cation exchange.
- The charges on the colloids are positive and the exchange is among negatively charged anions.
- The positive charges associated with the surfaces of kaolinite, iron and aluminum oxides, and allophane attract anions such as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ .



- Just as in cation exchange, *equivalent* quantities of  $\text{NO}_3^-$  and  $\text{Cl}^-$  are exchanged.
- The reaction can be reversed, and nutrient anions so released can be absorbed by plants

- AEC generally decreases with the increase in pH.



# Weathering and CEC/AEC Levels

