

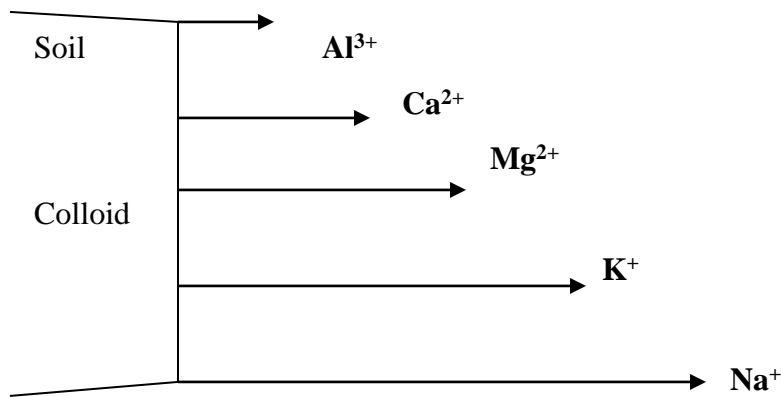
ION EXCHANGE

It is the interchange of ions between soil colloids and solution phases and/ or between the solid phases of soil if they are close in contact with each other. For the exchange of cations, the process is called cation exchange and for anions, it is known as anion exchange. These ions exchange reactions are reversible.

Soil Solution: Water having dissolved salts in the soil is called soil solution.

Distribution of soluble and exchangeable cations on the soil exchange complex:

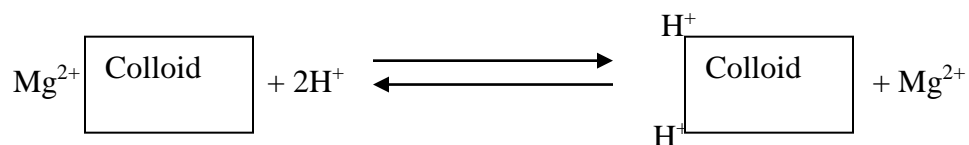
There is an excess of cations near the colloidal surface due to attraction by negatively charged surface. Parts of the cations are exchangeable because they neutralize the charge of the colloid. The remaining parts are soluble since they neutralize the charge of soluble anions. The effect of cation valence arises from the stronger attraction of higher charged cations by the colloid surface.



Distribution of cations on exchange surfaces of soil colloids

Cation Exchange

It is defined as the interchange between a cation in the soil solution and another cation on the surface of any surface active (negatively charged) soil particle such as clay colloid or organic colloid and between the two colloids if they are in close contact with each other. In this way, adsorbed cations can be replaced or exchanged with the cations in the soil solution by mass action (competition for the negative sites due to large number of ions present). An example of cation exchange is as under:



CHARACTERISTICS OF CATION EXCHANGE REACTIONS

- a) Exchange of cations between colloidal surface and soil solution takes place in equivalent amounts. It means that exchange reactions are stoichiometric in nature, e.g. two H^+ ions are required to replace one Mg^{2+} ion.
- b) Cation exchange reactions take place at a rapid speed.
- c) Cation exchange reactions are reversible in nature.
- d) Highly charged cations tend to be held more strongly than those which are less highly charged.
- e) Adsorbed cations can be exchanged by other cations in soil solution by mass action. So the concentration of a cation in the soil solution influences the exchange reaction. If one cation dominates, it will be favoured in the exchanged reaction, regardless of its size or charge.

Law of Mass Action: This law tells that an exchange reaction will proceed in the right direction, if the released ion is prevented from reacting in the reverse direction.

Cation Exchange Capacity (CEC):

Cation exchange capacity of a soil can be defined as the sum total of the exchangeable cations that a soil can adsorb. CEC of soil is expressed as $cmol_c kg^{-1}$.

Factors Affecting CEC of Soil:

Important factors affecting CEC of soil are as under:

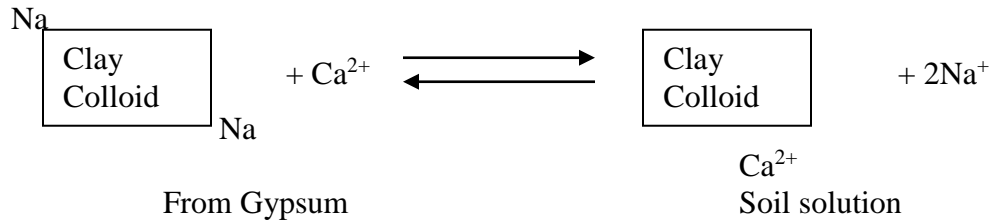
- a) **pH:** CEC of a soil changes with a change in pH. As pH rises, pH dependent CEC also increases. Most CEC from humus is pH dependent and hence, up to 10-40 % of soil' CEC may be from pH dependent sites. As pH is raised, negative charges on 1: 1 type clays, allophanes, humus and even Fe, Al oxides increases, thereby increasing the CEC. Commonly CEC is determined at a pH of 7.0 or 8.2. At neutral or slightly alkaline pH, CEC reflects most of the pH dependent charges as well as permanent ones.
- b) **Amount of Clay:** CEC of soils generally increases with the increase in clay contents. For every 1 % clay, a CEC value of 0.5 can be established. e.g., if a soil has 40 % clay, CEC contributed by this clay content will $(40 \times 0.5) 20 cmol_c kg^{-1}$.
- c) **Type of Clay:** Soils having 2: 1 clays (smectite) have a higher CEC than those that have 1: 1 clays like kaolinite because smectite clays have more isomorphous substitution than kaolinite clays.
- d) **Amount of organic matter:** Soils having large amounts of organic matter have more CEC than those that have the same amounts and types of clays but less organic matter. For every 1 % well decomposed organic matter (humus) in soil, a CEC value of 2 can be

established. e.g., if a soil has 5 % organic matter, CEC contribution by this organic matter amount will be $10 \text{ cmol}_c\text{kg}^{-1}$. For a soil having 40 % clay and 5 % organic matter, CEC value will be $30 \text{ cmol}_c\text{kg}^{-1}$.

Significance of CEC for nutrient availability:

Cation exchange is an important character because the exchangeable cations held on the exchange complex are available to plants, supplement the small quantity in solution and are retained in soils and not lost with leaching water. By cation exchange, hydrogen ions from the root hairs and microorganisms replace nutrient cations from soil exchange complex. The replaced nutrient cations go to the soil solution where they can be adsorbed by the plant roots and microbes or they may be lost by leaching. Importance of CEC for nutrient availability to plants is as under:

1. Cation exchange is an important reaction in soil fertility. e.g.,
 - a. Exchangeable + soluble K is major source of K to plants. A CEC measurement of exchangeable K indicates whether K should be applied to soil in the form of fertilizer or not.
 - b. The exchangeable Mg is often a major source of plant Mg. The plant nutrients like Ca, Mg and K are supplied to plants in large amounts from exchangeable forms.
 - c. Cation exchange sites hold Ca^{2+} , Mg^{2+} , K^+ , Na^+ and NH_4^+ ions and slow their losses by leaching, i.e., soils with high CEC have less leaching losses of these cations.
 - d. Cation exchange sites hold fertilizer K^+ and NH_4^+ and greatly reduce their mobility in soils.
2. It is an important reaction in causing and correcting soil acidity and alkalinity. Liming a soil to correct soil acidity is a cation exchange reaction. The amount of lime required to raise pH of an acidic soil is greater as CEC is greater.
3. Cation exchange is also greater as a mechanism in purifying and altering percolating water. Cation exchange sites adsorb many metals like Cd^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} that might be present in waste waters. Adsorption of cations on the exchange complex removes them from waste waters, thereby purifying waters.
4. Cation exchange is also an important reaction in altering soil physical properties. A sodium saturation percentage of over about 15 can cause poor soil structure. It is reclaimed by applying gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).



Application of gypsum which is a source of Ca^{2+} , to replace Na^+ from the clay complex is a good example of cation exchange in improving physical properties of soil.

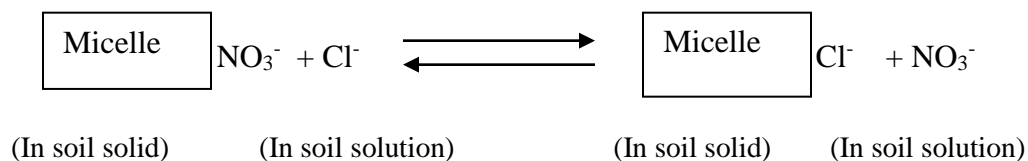
ANION EXCHANGE

It is defined as the interchange between an anion in the soil solution and another anion on the surface of any surface active (positively charged) soil particle such as clay colloid or organic colloid and between the two colloids if they are in close contact with each other.

ANION EXCHANGE CAPACITY (AEC)

The sum total of exchangeable anions that a soil can adsorb is called anion exchange capacity of soil and is expressed as $\text{cmol}_c \text{ kg}^{-1}$ of soil.

Positive charges associated with hydrous oxides of Fe & Al, some 1: 1 type clays and amorphous materials like allophone make possible the adsorption of anions. In turn, these anions, just like cations replace each other. The anion exchange that takes place is important as a means of providing readily available nutrient anions to higher plants. The basic principles of cation exchange apply to anion exchange, except that the charges on the colloids are positive and the exchange is among negatively charged anions. A simple example of an anion exchange reaction is as below:



Just as in cation exchange, equivalent quantities NO_3^- of Cl^- and are exchanged, reaction can be reversed and plant nutrients can be released for plant adsorption. So it can be said that anion exchange is an important mechanism for interactions in the soil and between soil & plants. Together with cation exchange, it largely determines the ability of soils to provide nutrients to plants promptly.

BASIC CATION SATURATION PERCENTAGE

The proportion of CEC occupied by a given cation is known as its cation saturation percentage. Among the various cations adsorbed on the clay complex, H^+ and Al^{3+} are the acidic cations as aluminum ions on the exchange complex also give an acidic reaction. In acidic soils, H^+ and Al^{3+} ions dominate

while in alkaline soils Ca^{2+} , Mg^{2+} , Na^+ , K^+ and NH_4^+ ions dominate and represent the major portion of CEC. The proportion of basic cations expressed on percentage basis to the total cations on the cation exchange complex is called as basic cation saturation percentage (BCSP) of soil. It can be calculated as:

$$\text{BCSP} = \frac{\text{Sum of basic cations}}{\text{CEC}} \times 100$$

A high basic cation saturation percentage is usually desirable. A direct correlation between soil pH and BCSP exists. The more acidic a soil is, the lower the percentage of basic cation saturation. Most soils are generally 100 % basic cation saturated at pH 7 or higher. The pH used for cation exchange and CEC determination must be specified whenever this concept is to be used.

IMPORTANCE OF BCSP

The basic cation saturation percentage is useful for soil genesis and classification purposes. It is a criterion of soil taxonomy in the United States Soil Classification Scheme.

Saturation does not provide much information that is not already available from pH values. However, it does provide numerical values of the amount of exchangeable Al and H ion species which helps in predicting the amount of lime required to neutralize soil acidity. Soils having more basic cation saturation percentage are generally more fertile than having lower percentage.