

The important functional groups are carboxylic (COOH) phenolic (C<sub>6</sub>H<sub>4</sub>OH), enolic (-OH) and imide (=NH) etc.

#### Differences between organic and inorganic colloids

PROPERTY	ORGANIC COLLOIDS	INORGANIC COLLOIDS
Origin	Decomposition of organic matter	Weathering of rocks and minerals
Composition	C, H, O (N, P, S)	Si, Al, Fe, Mg, O, OH
Shape	Amorphous	Crystalline except allophone and sesquioxide clays
Stability	Unstable in nature	Stable
Origin of charge	pH dependant	Mostly due to isomorphous substitution and partly by soil reaction
CEC	150-400 cmol kg <sup>-1</sup>	3-150 cmol kg <sup>-1</sup>
Water and nutrient holding capacity	High	Low
Plasticity	Low	High
Surface area m <sup>2</sup> /g	Around 900	Variable (10 to >700)

## LECTURE 24

### ORIGIN OF CHARGE ON SOIL COLLOIDS

The two properties that mostly account for the reactivity of soils are surface area and surface charge. Surface area is the direct result of particle size and shape. Charge development in soils is intimately associated with clay sized particles and humus.

Two types of charge arises on inorganic colloids i.e., permanent charge or constant charge, temporary charge or variable charge.

## Permanent charge

### Isomorphous substitution

Substitution of one ion with another ion of comparable size (within 15 %) and charge variation of one unit without disturbing the crystal lattice.

The weathering of wide variety of rocks and minerals permits cations of comparable size to substitute for silicon, aluminum and magnesium ions in the respective tetrahedral and octahedral sheets. Aluminum (0.051 nm) is only slightly larger than silicon (0.042 nm). Consequently the aluminum can fit in to the centre of the tetrahedron in the place of the silicon without changing the basic structure of the crystal. This process is called "Isomorphous substitution", which is common and accounts for the wide variability in the nature of silicate clays. It is of vital importance because it is the primary source of both negative and positive charges of silicate clays.

Isomorphous substitution also occurs in the octahedral sheet. Iron ( $\text{Fe}^{3+}$  -0.064 nm) and zinc (0.074 nm ( $\text{Fe}^{2+}$  0.070 nm) can fit in to the position of either aluminum or magnesium (0.06), as a central ion in the octahedral sheet.

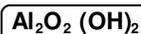
Isomorphous substitution is responsible for development of permanent charge on inorganic colloids. The isomorphous substitutions have taken place slowly through past weathering cycles, and are not subject to easy modification. Consequently, these charges are termed constant or permanent charges, because they are related to the chemical composition of silicate clays.

In the process of substitution, the substituting ion may have a greater, equal or lower charge and size than the ion for which it substitutes. The difference in dimensions of substituted ions was reported to be no more than 15% and the valency difference between the substituting ions should not be more than one unit (Paton, 1978).

#### Tetrahedral sheet



#### Octahedral sheet



No substitution

#### Al substituted for Si

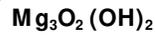


#### Mg substituted for Al

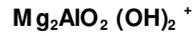


substitution resulted in negative charge

Isomorphous substitution can also be a source of positive charge. If  $\text{Al}^{3+}$  ion substitutes for  $\text{Mg}^{2+}$  ion, a net positive charge results. Such positive charges are characteristic of the trioctahedral sheet in some vermiculites and chlorites.



**Trioctahedral sheet**



**net positive charge because**

**$\text{Al}^{3+}$  substituted for  $\text{Mg}^{2+}$**

Though there is a scope for development of both positive and negative charges on silicate clays, the net charge is always negative because most of the substitutions lead to the development of negative charges, which far outweigh the positive charges.

#### **TEMPORARY CHARGE ON COLLOIDS**

It is the second source of charge on some silicate clays (kaolinite) and on humus, allophone and Fe, Al hydroxides. Because these charges are “pH dependant”, they are termed “variable, temporary and pH dependant” charges.

The positive charge developed at low pH and the excess negative charge developed at high pH, are collectively known as pH dependant charges. The soil’s total charge is the algebraic sum of its positive and negative charges.

The zero point charge (ZPC) has been used as an index of the positive and negative charges on soil colloids. The ZPC is the pH at which negative and positive charges of a colloid are equal.

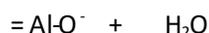
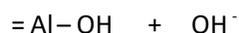
The contribution of edge OH groups on crystal edges or on exposed planes gives rise to charge on certain colloids. At high pH, hydrogen of  $\text{OH}^-$  on crystal lattice dissociates and combines with hydroxyl ions to form water molecules. This leaves negative charge on colloidal surface. At low pH protonation of exposed hydroxyl groups results in positive charge development. dependant charge is related both to the acidity of the edge groups and to the area of the edge surface. In 2:1 type minerals, edge surface is small relative to the basal plane. Kaolinites tend to stack in C-dimension, increasing the relative area of edges in relation to basal plane area. For these reasons, pH dependency of charge is more important for kaolinite than for smectites or vermiculite.

2:1 type minerals

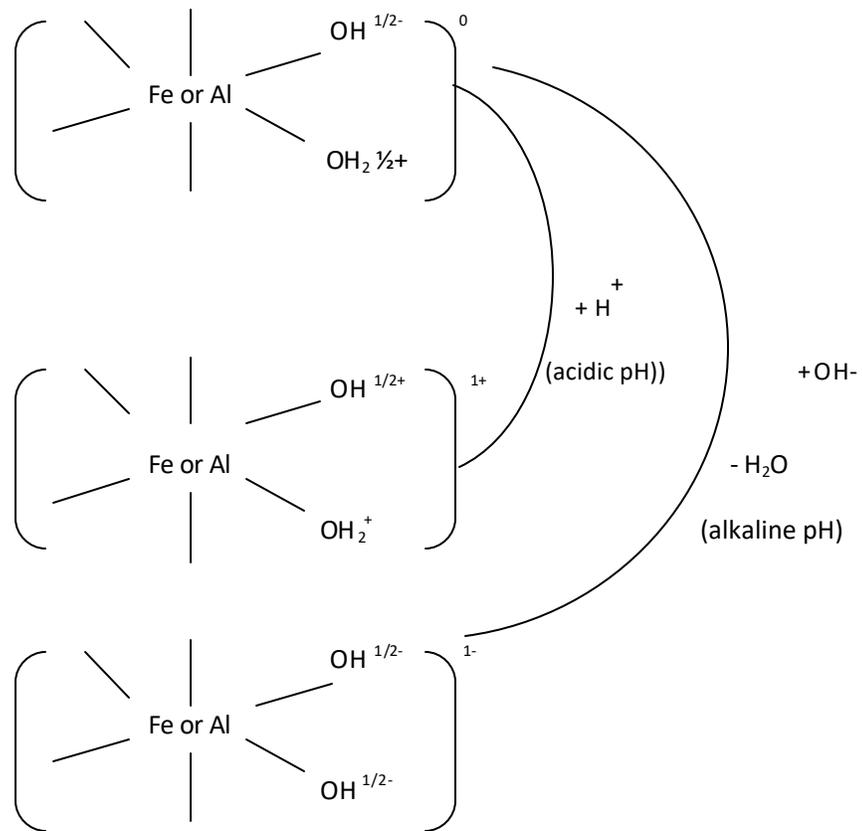
5-10% pH dependant charge

1:1 type mineral

50%



Development of positive and negative charges on crystal edges:



**Organic colloids:** The primary source of charge on organic colloids is considered to be the gain or loss of H<sup>+</sup> from functional groups on the surface of colloids. The functional groups include hydroxyl (-OH), carboxyl (-COOH), phenolic (-C<sub>6</sub>H<sub>4</sub>OH) and amine (-NH<sub>2</sub>). The charge that develops from such groups depends largely on the pH of the ambient solution, which regulates the degree of protonation or deprotonation of the group.



The soil colloids that are capable of developing pH dependant charge include layer silicates, oxides and hydroxides of Fe and Al and organic matter.

	Negative charge			
	Total	Constant%	Variable%	
Organic	200	10	90	0
Montmorillonite	100	95	5%	0
Illite	30	80	20	0
Kaolinite	8	5	95	2
Gibbsite	4	0	100	5
Goethite	4	0	100	5

## LECTURE 25

### ION EXCHANGE IN SOILS

Ion exchange is defined as a reversible process by which cations and anions are exchanged between solid and liquid phases and between solid phases, if in close contact with each other.

Adsorption is defined as a phenomenon by which an increase in concentration or an accumulation of an ion on a solid occurs due to ion exchange or other reactions. Desorption is a phenomenon by which the replacement or release of an adsorbed ion species occurs.

Ion exchange property is almost entirely to the clay and silt fractions and the organic matter. The soil particles are amphoteric in nature and soil particles have the power to hold both cations and anions. The charge density and potential are higher on edges and corners and in furrows and cavities as compared to flat (plane) surfaces and consequently in exchange phenomena are probably concentrated more in those sites.

The exchangeable ions are held to the surface by coulomb forces and van-der-waal's forces. In most of the soils the exchangeable cations are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$ , of which  $\text{Ca}^{2+}$  is the dominant exchangeable ion. In strong acid soils  $\text{Al}(\text{OH})_2^+$  may act as a dominant exchangeable ion. In alkali soil  $\text{Na}^+$  becomes dominant and the most common anion  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  etc