

Basics of Clay Minerals and Their Characteristic Properties

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Abstract

Clay minerals such as kaolinite, smectite, chlorite, micas are main components of raw materials of clay and formed in presence of water. A large number of clays used to form the different structure which completely depends on their mining source. They are known as hydrous phyllosilicate having silica, alumina and water with variable amount of inorganic ions like Mg^{2+} , Na^+ , Ca^{2+} which are found either in interlayer space or on the planetary surface. Clay minerals are described by presence of two-dimensional sheets, tetrahedral (SiO_4) and octahedral (Al_2O_3). There are different clay minerals which are categorized based on presence of tetrahedral and octahedral layer in their structure like kaolinite (1:1 of tetrahedral and octahedral layers), smectite group of clay minerals (2:1 of tetrahedral and octahedral layers) and chlorite (2:1:1 of tetrahedral, octahedral and octahedral layers). The particle size of clay minerals is <2 microns which can be present in form of plastic in presence of water and solidified when dried. The small size and their distinctive crystal structure make clay minerals very special with their unique properties including high cation exchange capacity, swelling behavior, specific surface area, adsorption capacity, etc. which are described in this chapter. Due to all these unique properties, clay minerals are gaining interest in different fields.

Keywords: Clay minerals, cation exchange capacity, swelling capacity, adsorption, tetrahedral

1. Introduction

Georgius Agricola (1494–1555), the founder of geology, was seemingly the first who gave the definition of clay in 1546. It has been modified several times due to which the clay definition raises the questions related of constituents of clay and implicitly which was very important [1]. The latest effort to solve all these issues was done by the Joint Nomenclature Committees (JNCs) of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS). According to these societies, clay, a naturally occurring material, composed mainly of fine-grained minerals, become plastic in presence of water and become hard when dried or fired. By this definition of clay, engineered clays and clay-like materials can be distinguished as clay (fine grained minerals) exhibiting plasticity in presence of water and become hard on drying and firing [2, 3].

1.1 Clay

Clay is a soft, freely bound, fine grained natural rock or earthy material having diameter less than 0.005 mm and composed essentially of clay particles. Based on

the standard definition of mineral, clays are mainly inorganic materials except peat, muck, some soils, etc. that contain huge amount of organic/natural materials. The clay particles are formed due to the weathering and erosion of rocks containing soil, ceramic clays, clay shales, glacial clays (including great volume of detrital and transported clays) the mineral group feldspar (known as the 'mother of clay') over vast spans of time. During weathering, the content of feldspar is distorted by hydrolysis process results in formation of clay minerals such as kaolinites (the primary minerals in kaolin clays) and smectite (the primary minerals in bentonite clays). Clay can incorporate with one or more clay minerals even in presence of minute quantities of quartz (SiO_2), metal oxides (Al_2O_3 , MgO etc.) and organic matter [4, 5]. The plasticity of clays are due to their particle size, geometry as well as content of water and become hard, stiff, coherent and non-plastic upon drying or firing. Plasticity and hardness are greatly affected by the chemical composition of the material present in the clay. Clays can be molded in any form when they retain water. For example, some species of chlorite and mica are found to be non-plastic while grinding macroscopic flakes even where more than 70% of the material is $<2 \mu\text{m}$ esd (equivalent spherical diameter). Whereas some species of chlorites and micas become plastic on grinding the macroscopic flakes where 3% of the materials is $<2 \mu\text{m}$ esd. Clays are easily molded into a form that they retain when dry, and they become hard and lose their plasticity when subjected to heat

In all definition of clays, the particle size is a key parameter, no generally upper limit is accepted till now. Although clays can be distinguished from other fine-grained soils on the basis of their size difference and mineralogy. The particle sizes of silts (fine-grained soils that do not consist of clay minerals) is larger than clays. Individual clay particles are always smaller than 0.004 mm. The difference between silt and clay varies by discipline. Geologists and soil scientists usually consider a particle size of $2 \mu\text{m}$ (clays being finer than silts) for the separation, sedimentologists apply $4\text{--}5 \mu\text{m}$, and colloid chemists use $1 \mu\text{m}$ [6]. According to Geotechnical engineers, differentiation between silts and clays can be done on the basis of the plastic characteristics of the soil, as measured by the soils' Atterberg limits. The combination of silts, sand and clay ($<40\%$) are called loam [7].

Mostly, geologic clay deposits composed of phyllosilicate minerals having variable amounts of water present in the mineral structure. The clay can appear in different form of colors from white to dull gray or brown to deep orange-red depending on the soil's content [4]. The colloidal suspensions are formed when clays are immersed in water and flocculation occurs when they immersed in saline water.

Clays are divided into two classes:

- a. Residual clay: Residual clays are found in the place of origin and formed by surface weathering which give rise to clay in three ways:
 - Chemical decomposition of rocks, such as granite, containing silica and alumina
 - Solution of rocks, such as limestone, containing clayey impurities, which, being insoluble, are deposited as clay
 - Disintegration and solution of shale [8].
- b. Transported clay, also known as sedimentary clay, removed from the place of origin by erosion and deposited in a new and possibly distant position.

1.2 Clay minerals

Clay minerals are the characteristic minerals on the earth found near planetary surface (the surface where the outer crust of the object comes in contact with atmosphere) environment with variable amount of ions like iron, magnesium, alkali metals, alkaline earth metals and other cations. They are considered as important constituents of soil and form by diagenetic and hydrothermal alteration of rocks in presence of water [9]. They are commonly found in fine grained sedimentary rocks such as shale, mudstone and siltstone. Clay minerals act as “chemical sponges” as they have capacity to hold water and dissolved plant nutrients eroded from other minerals due to the presence of some unbalanced electrical charge on their surface [8]. As water is essential for clay minerals formation, therefore, most of the clay minerals are known as hydrous aluminosilicate or hydrous aluminum phyllosilicate.

The formation of clay minerals is due to the chemical weathering of rock [9, 10]. The chemical and structural composition of clay minerals is found to be similar to the primary minerals which originate from the crust of earth mainly from igneous or metamorphic rocks. Transformations may occur in ambient conditions. Although some of the most resistant primary minerals such as quartz, micas and feldspar may remain in soils whereas other less resistant primary minerals (pyroxenes, amphiboles) are susceptible to breakdown by weathering, thus forming secondary minerals. The resultant secondary minerals are formed due to either modification of the primary mineral structure (incongruent reaction) or neof ormation through precipitation or recrystallization of dissolved constituents of primary minerals into a more stable structure (congruent reaction). These secondary minerals are most probably defined as phyllosilicates because, as the name suggest (Greek: phyllon, leaf), they exhibit a platy or flaky structure with irregular edges; while one of their most important basic structural units is an extended SiO_4 tetrahedra sheet [11].

As the clay minerals are most important component of the soil, they are usually ultra-fined particles having less than $2\ \mu\text{m}$ sized particles. Clay minerals are found to be the most interesting class of minerals that have attracted substantial worldwide attention and investment in research and development. In 1930, the nature of clay can be defined with advanced development in X-Ray diffraction technology used to investigate the molecular nature of clay particles.

Most of the chemical and physical properties of the soil including swelling - shrinking capacity, cation exchange capacity etc. are due to presence of the clay minerals in soil. Clay minerals are look like micas due to their chemical composition [12].

2. Structure and chemical composition of clay minerals

The properties that define the composition of clay minerals are derived from chemical compounds present in clay minerals, symmetrical arrangement of atoms and ions and the forces that bind them together. The clay minerals are mainly known as the complex silicates of various ions such as aluminum, magnesium and iron [13]. On the basis of the arrangement of these ions, basic crystalline units of the clay minerals are of two types:

- a. silicon – oxygen tetrahedron consists of silicon surrounding by four oxygen atoms and unite to form the silica sheet.
- b. aluminum or magnesium octahedron consists of aluminum surrounding by six hydroxyl units and combine to form gibbsite sheet (If aluminum is main dominating atom) or brucite sheet (If magnesium is main dominating atom) (**Figure 1**) [14].

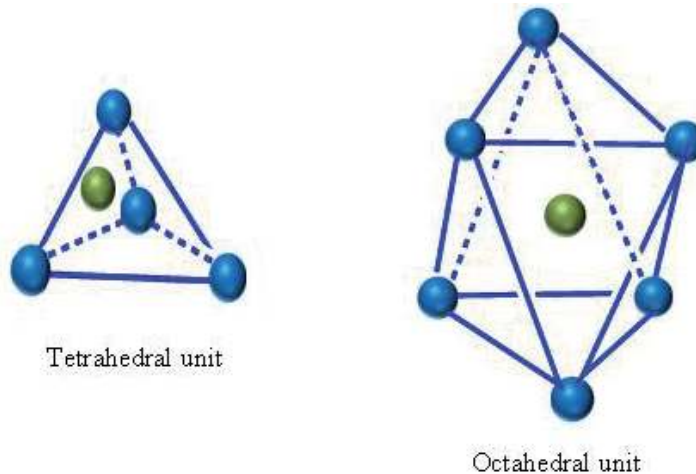


Figure 1.
Structure of tetrahedral and octahedral unit.

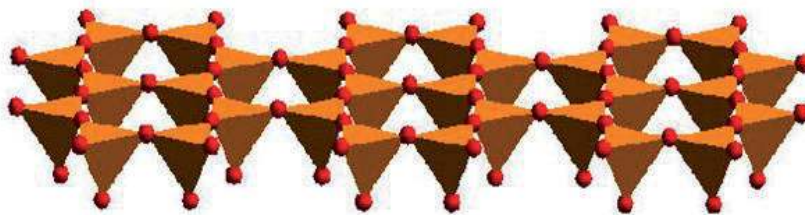


Figure 2.
Arrangement of tetrahedral unit to form the tetrahedral sheet.

2.1 Tetrahedral sheet

The main dominating atom in the tetrahedral sheet is found in form of Si^{4+} cation. The basic building block of tetrahedral sheet is a unit of Si atom surrounded by four oxygen atom known as silica tetrahedra. The tetrahedral sheet is formed by sharing of three oxygen of each tetrahedra with three nearest tetrahedra as shown in **Figure 2**. These oxygen atoms are known as basal oxygen which connect pairs of all tetrahedra together (more or less) in one plane whereas the fourth oxygen atom remain free and form the bond with other polyhedral elements known as apical oxygen. Apical oxygens are all in a separate plane and provide a link between both tetrahedral and the octahedral sheet [15]. As only one apical O is present per tetrahedron therefore, each tetrahedron shares a corner with an octahedron in the octahedral sheet.

The tetrahedral sheet is carrying negative charge due to the isomorphous substitution of Al^{3+} in place of Si^{4+} generating the charge deficiency in tetrahedral sheet. Common tetrahedral cations are Si^{4+} , Al^{3+} , and Fe^{3+} .

2.2 Octahedral sheet

The main dominating atoms in octahedral sheets are Al^{3+} or Mg^{2+} surrounded by six oxygen atoms or hydroxyl group give rise to eight sided building block known as octahedron. Since, octahedral sheet are present in two forms: dioctahedral or trioctahedral sheet.

- a. When aluminum having three positive valences present in the octahedral sheet, only two-thirds of the sites are filled so that the charges will be balanced which results in formation of dioctahedral sheet. When magnesium having two positive charge valences is present, all three positions are filled to balance the charge which results in formation of trioctahedral sheet [15]. Therefore, for di – octahedral sheet, Al_3^+ is the main dominating atom with $Al_2(OH)_6$ a unit cell formula and often abbreviated as the stoichiometric equivalent $Al(OH)_3$ where two Al_3^+ atoms coordinated with six oxygen/or hydroxyl ions

- b. In tri – octahedral sheet, Mg^{2+} is the main dominating atom where three Mg^{2+} atoms are coordinated with six oxygen/or hydroxyl ions having a unit cell formula of $Mg_3(OH)_6$ (also written as $Mg(OH)_2$). Gibbsite or hydrargillite (hydrous aluminum oxide, $Al_2(OH)_6$ or $Al_2O_3 \cdot 3H_2O$) and brucite (hydrous oxide of magnesium, $Mg(OH)_2$) are the minerals which are generally described in literature on clay chemistry, mineralogy and structure. The octahedral sheet is formed by sharing of two oxygen of each octahedra when various octahedra linked together horizontally (**Figure 3**) [16, 17].

2.3 Isomorphous substitution

The difference in the composition of clay minerals occurs very frequently when substitution of ions takes place within the mineral structure. The substitution of Si^{4+} , Al^{3+} , and Mg^{2+} takes place with other cations with comparable ionic radii in their respective tetrahedral and octahedral sheets due to weathering (**Table 1**). Consequently, in the center of the tetrahedron, replacement of Si^{4+} by Al^{3+} without changing the basic structure of the crystal takes place. Moreover, in octahedron, Al^{3+} and Mg^{2+} cations are replaced by the ions such as $Fe^{3+/2+}$ and Zn^{2+} (ionic radius = 0.074 nm). This process is known as isomorphous substitution where one structural cation is replaced by another of similar size and this kind of replacement signifies the primary cause of both negative and positive charges in clay minerals. For example, the substitution of one Al^{3+} for a Si^{4+} in the tetrahedral unit creates one negative charge. Alternatively, replacement of a lower valence cation by a higher valence (Fe^{2+} by Fe^{3+}) cation results in a gain of one positive charge. The net charge of the clay mineral is determined by after balancing electron loss and gain within the structure. In most soils, the net negative charge exceed by a positive charge after substitution [18].

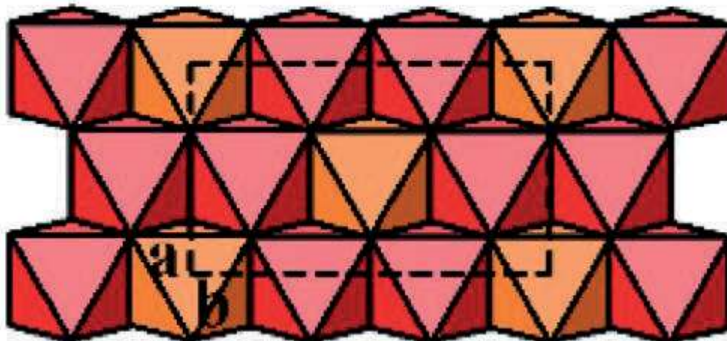


Figure 3.
Arrangement of octahedral unit to form the octahedral sheet.

Cation-exchange capacities and specific surface areas of clay minerals		
mineral	cation-exchange capacity at pH 7 (milliequivalents per 100 grams)	specific surface area (square metres per gram)
kaolinite	3–15	5–40
halloysite (hydrated)	40–50	1,100*
illite	10–40	10–100
chlorite	10–40	10–55
vermiculite	100–150	760*
smectite	80–120	40–800
palygorskite-sepiolite	3–20	40–180
allophane	30–135	2,200
imogolite	20–30	1,540

*depending on the fraction of internal specific surface area.

Table 1.
Cation exchange capacity and specific surface area of different clay minerals.

3. Classification of clay minerals

The aluminosilicate layers comprises of the basic structural units of phyllosilicates which is formed by the combination of tetrahedral and octahedral sheets bound by shared oxygen atoms. Both the tetrahedral and octahedral sheets are the main components of phyllosilicates (due to their leaf like or plate like structure, they are known as phyllosilicates) which bound together by sharing of oxygen atoms into different layers. Phyllosilicate are the most common clay minerals consists of Si dominating tetrahedral unit and Al/or Mg dominating octahedral unit which are arranged in to sheet form. Based on number of tetrahedral and octahedral sheets and their arrangement, the phyllosilicates are divided into following categories including layer and chain silicates, sesquioxide and other inorganic minerals:

Clay can be classified depending on the way that the tetrahedral and octahedral sheets are packed into layers. The major groups of clay minerals present in the soil environment include layer and chain silicates, sesquioxides, and other inorganic minerals as shown in **Figure 4** [19].

3.1 Layer silicates

A silicate comprising of planar octahedral layer bound to tetrahedral layer above and below with a distinctive repeating distance between t-o-t layers. These are the primary component of soils and are known as excellent trappers of water held between layers. Minerals within these groups are further categorized into dioctahedral and trioctahedral [11]. On the basis of number and arrangements of tetrahedral and octahedral sheets present in clay, the layer silicate are divided into three categories:

- (a) 1:1 type of clay mineral
- (b) 2:1 type of clay mineral
- (c) 2:1:1 type of clay mineral

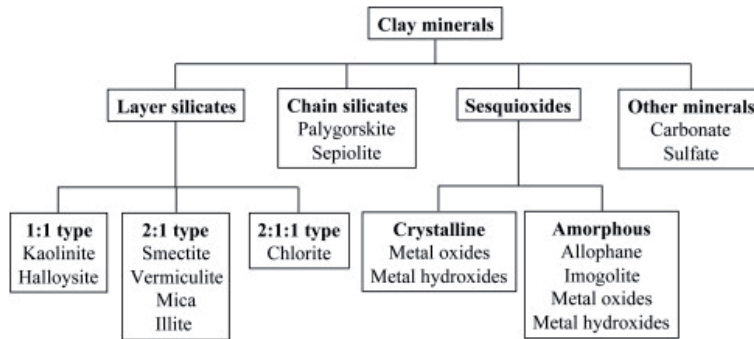


Figure 4.
 Classification of clay minerals.

3.1.1 1:1 Layer silicate

Each individual layer is assembled from one tetrahedral (SiO_4) and one octahedral sheet (AlO_6). The sheets are bonded together by sharing of O^{2-} ions. Kaolinite and Halloysite are examples under this category [20].

Kaolinite is a 1:1 clay mineral with chemical formula $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$. The rocks that are found to be rich in Kaolinite are identified as Kaolin or china clay [21]. Kaolinite is derived from the kaolin which is very common and is a corruption of the Chinese Jailing (Pinyin; Wade-Giles romanization Kao-ling), meaning “high ridge,” [22]. The chemical weathering of aluminum silicate such as feldspar results in formation of a soft, usually white, earthy mineral (dioctahedral phyllosilicate clay) The dickite and nacrite are rare forms of kaolinite which are chemically similar to kaolinite but amorphous in nature. Kaolinite is found to be electrostatically neutral having triclinic symmetry. The hydrogen bonding is found in between oxygen atoms and hydroxyl ions of the layers that are paired. Since, hydrogen bonding is weak, random movements between the layers are quite common results in lower crystallinity of kaolinite minerals than that of the triclinic kaolinite. The ideal structure of kaolinite has no charge. Hence, the structure of Kaolinite is fixed due to the hydrogen bonding therefore; there is no expansion between the layers or have low shrink-swell capacity when clay is wetted. Kaolinite does not swell in water and have low surface areas and cation exchange capacity (< 1 centimole/kg). Due to the low surface area and little isomorphous substitution, Kaolinite has low capacity to adsorb the ions [15]. Kaolinite composite layers are 7 \AA thick and the c-axis/interlayer spacing is also of 7 \AA . Dickite and nacrite are polytypic forms of kaolinite consisting of a double 1:1 layer and have monoclinic symmetry. Dickite and nacrite differentiate themselves by different stacking sequences of the two 1:1 silicate layers [23].

The mineral Halloysite having 1:1 layer structure as kaolinite has a single sheet of water molecules between two layers with c-spacing/interlayer spacing 10.1 \AA which make it different from kaolinite. It is illustrated by its tubular form in contrast to the platy form of kaolinite particles. Dehydration occurs on mild heating of Halloysite and will irreversibly get transformed to kaolinite. Halloysite possesses a hydrated form with a composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. which irreversibly changes to a dehydrated variety mainly at relatively low temperatures (60°C) or upon being directed to conditions of low relative humidity. The dehydrated form of Halloysite has basal spacing with thickness of a kaolinite layer (approximately 7.2 \AA) whereas the basal spacing of hydrated form is about 10.1 \AA . The difference of 2.9 \AA is due to the thickness of a sheet of water. Consequently, in hydrated form, the layers of halloysite are separated by monomolecular water layers that are lost during dehydration [23].

Serpentine: Serpentine is a group of hydrous magnesium-rich silicate minerals and a common rock-forming mineral having the composition $Mg_3Si_2O_5(OH)_4$ [24]. Serpentine generally appears in three polymorphic forms: chrysotile, a fibrous type used as asbestos; antigorite, a variety exists in either corrugated plates or fibers; and lizardite, a very fine-grained, platy variety. Serpentine is usually grayish, white, or green (due to iron replacing magnesium) but may be yellow (chrysotile) or green-blue (antigorite). The formation of Serpentine takes place below 500°C (930°F) by either addition of water or sometimes silica to various magnesium silicates—e.g., forsterite or enstatite [25]. It usually occurs along the crests and axes of great folds, such as island arcs or Alpine mountain chains. Normal occurrences are in altered peridotites, dunitites, or pyroxenites; serpentinite is a rock consisting largely of serpentine.

3.1.2 2:1 Type of clay mineral

Most of the layer silicate clays are commonly found in soils and based on the mica structure in which a single octahedral sheet sandwiched between two tetrahedral sheets and form an individual composite layer as shown in **Figure 5**. Therefore, they are referred as 2:1 layer silicates in which Talc [$Mg_3Si_4O_{10}(OH)_2$] and Pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] signifies the trioctahedral and dioctahedral members. In dioctahedral and trioctahedral layer silicates, two and three octahedral sites are occupied respectively out of the three available sites in the half-unit cell (single Si_4O_{10}) [26].

These types of clay minerals consist of one octahedral layer sandwiched between two tetrahedral layers. They are further characterized into two categories:

A. Expanding clay minerals: Smectite group and Vermiculite

B. Non – expanding clay minerals: illite (mica groups)

A. **Expanding clay minerals:** This group includes mainly smectite group of clay minerals and vermiculite clay mineral. They are known for their interlayer expansion which happens during their swelling behavior when they are wet.

Smectites are mainly based on either trioctahedral 2:1 (talc) or dioctahedral 2:1 (Pyrophyllite) structure and differ from these neutral structures due to the presence of isomorphous substitution in the octahedral or tetrahedral layer. The **Smectite** group of clay minerals are further divided into Saponites (trioctahedral) and Montmorillonite (dioctahedral). Another important member of the Smectite family is **Bentonite**. Bentonite clay is also known as sedimentary clay and has unique property of water retaining.

The most prominent members of this group are Montmorillonite, Beidellite, nontronite, and saponite. The flake-like crystals of smectite (e.g., Montmorillonite) are consisting of an expanding lattice, 2:1 type clay mineral. Each layer is composed an octahedral sheet sandwiched between two tetrahedral (silica) sheets. Slight attraction is found between oxygen atoms present in the bottom tetrahedral sheet of one unit and in the top tetrahedral sheet of another unit. This allows a variable space between layers, which is occupied by exchangeable cations and water. Therefore, the exchangeable cations and water can easily enter the interlayer space resulting in the expansion of layers that may vary from 9.6 \AA to 20 \AA [14]. In Montmorillonite, magnesium ions are replaced aluminum ions in some sites of octahedral sheet and likewise, some silicon ions in the tetrahedral sheet may be replaced by aluminum ions. This type of replacement is known as isomorphous substitution which give rise

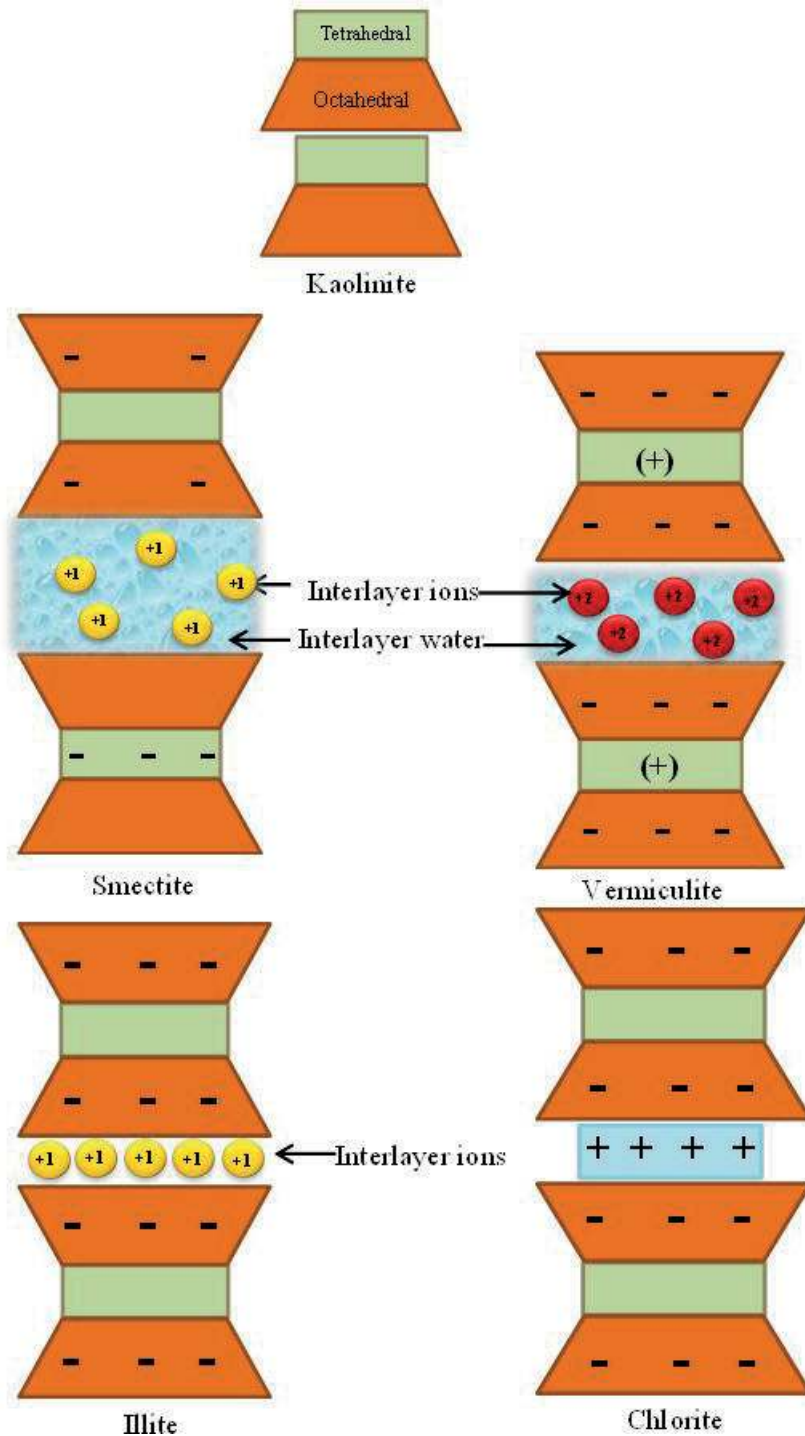


Figure 5.
 Different types of clay minerals.

to a negative charge on the surface of clay minerals. The magnitude of the negative charge depends upon the number of substituted atoms/ions. These negative charges of the unit cell are typically balanced by exchangeable hydrated alkali (Li, Na, K, Rb, Cs, Fr) or alkaline earth (Be, Mg, Ca, Sr, Ba, Rd) cations. Therefore, the

layer charge density of these minerals is found to be in between 0.2–0.6 per unit formula [27]. The general structural formula of smectite group of clay minerals is $(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot (\text{H}_2\text{O})_n$. The structure, chemical composition, exchangeable ions are responsible for their several unique properties such as high cation exchange capacity, high surface area and high adsorption capacity.

The quantity of cations required to balance the charge deficiency induced by these substitutions is referred to as the cation exchange capacity (CEC). The CEC for Montmorillonite ranges from 80 to 100 milliequivalent per 100 grams. Montmorillonite clays have very poor thermal stability.

These minerals show some prominent characteristics like high cation exchange capacity, swelling and shrinkage capacity. When smectite dominated soils (e.g., Vertisols) undergo dryness, wide cracks commonly appears making the soil difficult to till due to their hardness [28].

Bentonite: Bentonite is an impure form of aluminum phyllosilicate clay consisting 98% of montmorillonite and produced by in-situ divitrification of volcanic ash or by mechanical and chemical weathering of the parent rock, most often in the presence of water. Bentonite was found in the Cretaceous Benton Shale near Rock River, Wyoming (Bentonite, wikipedia). Chemical composition of the unit cell has been represented as $[(\text{Si}_{8.0})(\text{Al}_{3.02}\text{Mg}_{0.50}\text{Ca}_{0.06}\text{Fe}_{0.18}\text{T}_{i0.02}\text{Na}_{0.22})\text{O}_{20}(\text{OH})_4]$. It is a versatile mineral due to its platelet structure. The platelet consisting of a tetrahedral silicon oxide layer in which some silicon replaced by trivalent cations sandwiched between two octahedral aluminum oxide layers in which aluminum replaced by divalent cations. The hydroxide group is present on the edge of each platelet results in thixotropic nature [28].

The different types of bentonite are found based on their respective dominant element, such as potassium (K), sodium (Na), calcium (Ca), and aluminum (Al). For industrial purposes, three main classes of bentonite exist: sodium, calcium and potassium bentonite.

Sodium bentonite: Sodium bentonite expands in wet condition where it absorb the water as much as several times its dry mass. Because of its excellent colloidal properties, [29]. It is often used in drilling mud for oil and gas wells and also in boreholes for geotechnical and environmental investigations [30]. Due to its swelling capacity, sodium bentonite is used as a sealant, since it offers a self-sealing, low permeability barrier. Enhancement in some rheological or sealing performance are observed after various surface modifications of sodium bentonite for example, the addition of polymers [31].

Calcium bentonite: Calcium bentonite is considered as a useful adsorbent for ions, fats and oils [32]. It is known as the main active component of fuller's earth, probably one of the earliest industrial cleaning agents. Calcium bentonite can be converted to sodium bentonite (termed sodium beneficiation or sodium activation) by ion exchange process and show many of sodium bentonite's properties. In simple form, add 5–10% of a soluble sodium salt such as sodium carbonate to wet bentonite followed by mixing and allow the mixture to leave for a certain time so that the ion exchange take place. Hence, some properties of sodium-beneficiated calcium bentonite (or sodium-activated bentonite) such as viscosity and fluid loss of suspensions may not be fully comparable to those of natural sodium bentonite [30, 33].

Potassium bentonite: This is also known as potash bentonite or K-bentonite. Potassium bentonite is formed from alteration of volcanic ash and considered as potassium-rich illitic clay.

Vermiculite: Vermiculite also belongs to 2:1 group of clay minerals where one octahedral sheet occurs between two tetrahedral sheets. Most of the Vermiculites are Al dominated showing dioctahedral structure. Vermiculite is known as hydrous phyllosilicate mineral which undergoes substantial expansion when heated

results in exfoliation and commercial furnaces can routinely generate this effect. Vermiculite formed by the weathering or hydrothermal modification of biotite or phlogopite [34]. Vermiculite was first described in 1824 in Millbury, Massachusetts. Its name is derived from Latin word, *vermiculare*, “to breed worms”, for the manner in which it exfoliates when heated (Vermiculite,). In Vermiculite clay mineral, tetrahedral sheet is highly negatively charged due to the more substitution of Al^{3+} in place of Si^{4+} results in high layer charge density (in between 0.6–0.8 per unit formula) which is higher than smectite group of clay mineral [35]. The chemical formula of Vermiculite is $(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+})_3(\text{SiAl})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. The water molecules are present along with Mg^{2+} and other ions in the interlayer space instead of K^+ ion which makes it different from micas. Therefore, both the tetrahedral and octahedral units are joined together tightly rather than driving apart from each other resulting the less expansion of interlayer spacing on wetting [36]. The cation exchange capacity of Vermiculite is very high (100–150 meq/100 g). Vermiculite clays are weathered micas where the potassium ions are replaced by magnesium and iron ions between the molecular sheets [9, 37].

B. Non-expanding clay minerals: This group includes mainly Mica (illite) clay mineral which is a secondary form of mineral precipitate. This group is an example of a phyllosilicate, or layered alumino-silicate. Muscovite and biotite are also found in the clay fractions which are also called fine grained Mica. Illite is considered as an modified product of muscovite and feldspar formed from weathering and hydrothermal environments; known as component of sericite. It is commonly found in soil and argillaceous sedimentary rocks as well as in some low grade metamorphic rocks [38]. In illite, the tetrahedral sheet has more negative charge even higher than Vermiculite which is due to the presence of 20% of aluminum atoms in tetrahedral sheet in place of silicon atoms sites having considerable ion (isomorphic) substitution. The charge deficiency is mainly balanced by K^+ ions which are present in the interlayer space and act as bridge between the layers thus preventing the expansion of layers making them non - expanding. Therefore, the interlayer spacing is found to be 10 Å. The chemical formula is $(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})]$ [39]. The adsorption capacity, swelling, shrinkage capacity is less than Montmorillonite and Vermiculite but more than Kaolinite interstratified layers are present. The cation-exchange capacity (CEC) of illite is smaller than that of smectite but higher than that of kaolinite, typically around 20–30 meq/100 g [40].

3.1.3 2:1:1 Type of clay mineral

Chlorite is mainly belongs to 2:1:1 silicate group which are basically iron magnesium silicates with some aluminum atoms. The typical chlorite clay crystal composed of 2:1 layers, such as in vermiculites clay mineral alternate with a magnesium dominated tri-octahedral sheet (also known as brucite) giving rise to 2:1:1 ratio. All the octahedral positions in chlorite are occupied by magnesium ions as in the brucite layer [41]. The negative charge of chlorites is less than smectite or vermiculites but about the same as that of fine grained mica. There is no water adsorption between the layers responsible for the non – expanding nature of this crystal. The interlayer spacing is about 14 Å. Chlorites having a muscovite-like silicate layer and an aluminum hydroxide sheet are called donbassite and show the ideal formula of $\text{Al}_{4.33}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$ [22]. In many cases, the aluminum ions present in octahedral layer are partially replaced by magnesium ions as in magnesium-rich aluminum dioctahedral chlorites called sudoite. Another type of dioctahedral chlorite is Cookeite in which lithium substitutes for aluminum in the octahedral sheets [15, 42].

3.2 Chain silicates

3.2.1 Palygorskite or attapulgite

Palygorskite is a fibrous magnesium aluminum phyllosilicate having the formula $(\text{Mg, Al})_2\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4(\text{H}_2\text{O})$ which mainly found in a type of clay soil in the Southeastern United States. It is one of the types of fuller's earth [43]. The structure of palygorskite consists of extended silicon-oxygen sheets results in the retention of the mineral in the layer silicate family whereas the tetrahedral SiO_4 groups forming silicon-oxygen sheets are oriented in such a manner so that extended lathlike features could be developed which create the fibrous morphology. The chain silicate mineral found in sediments from playa lakes, saline deposits in desert soils and in calcareous material. Attapulgite is one type of palygorskite found in Attapulgas, Ga. For chemical formula and physical properties of attapulgite [44, 45].

3.2.2 Sepiolite

It is also known as Meerschaum, a fibrous hydrated magnesium silicate having chemical formula $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$. It is opaque and white, gray, or cream in color. It may seem like the bones of the cuttlefish Sepia. The name of Sepiolite is derived from cuttlefish Sepia.

The structures of sepiolite and palygorskite are almost similar consisting of narrow strips or ribbons of 2:1 layers that are attached to each other at the corners. One ribbon is attached to the another by inversion of the direction of the apical oxygen atoms of SiO_4 tetrahedrons; in other words, an extended rectangular box comprising of continuous 2:1 layers is enclosed to the nearest boxes at their extended corner edges. Therefore, due to the absence of silicate layers, channels or tunnels occur on the extended sides of the boxes results in the fibrous morphology of the minerals. Since the octahedral sheet is irregular, some of the magnesium ions present in octahedral layer are exposed at the edges and hold on bound water molecules (H_2O). In addition to the bound water molecules, variable amounts of zeolitic/free water (H_2O) are included in the rectangular channels. The width of the ribbons is found to be greater in sepiolite than in palygorskite which is a major difference between these chain silicates. The width of ribbons defines the number of octahedral cation positions per formula unit [5, 46].

3.3 Sesquioxide

Sesquioxide clays are produced from heavy rainfall and leached most of the silica and alumina from aluminosilicate clay by leaving less soluble iron oxide (Fe_2O_3), iron hydroxide ($\text{Fe}(\text{OH})_3$) and aluminum hydroxide ($\text{Al}(\text{OH})_3$). Sesquioxides of iron and aluminum are found in soil. A sesquioxide is an oxide comprising three atoms of oxygen and two another element. For example, aluminum oxide (Al_2O_3) is a sesquioxide. Many sesquioxides contain the metal atom having +3 oxidation state and the oxide ion such as Al_2O_3 , La_2O_3 except the alkali metal sesquioxides which contain both peroxide, (O_2^{2-}) and superoxide, (O_2^-) ions, e.g., Rb_2O_3 is formulated $[(\text{Rb}^+)_4(\text{O}_2^{2-})(\text{O}_2^-)_2]$ [45]. They are not adhesive in nature and do not swell in presence of water. They have ability to hold large amount of phosphate as they have tendency to hold phosphorous tightly make them unavailable for absorption by plants. They have low CEC. They are found in both crystalline and amorphous form. Crystalline Sesquioxide are either metal oxide or hydroxide whereas amorphous Sesquioxide are Allophane and Imogolite.

- A. **Imogolite** is an aluminosilicate having the composition of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$. In 1962, this mineral was discovered in a soil obtained from glassy volcanic ash known as “imogo.” Electron-optical observations of imogolite suggest a unique morphological feature with smooth and curved threadlike tubes differing in diameter from 10 to 30 nanometers which can further extend upto several micrometers in length. The shape of imogolite is cylindrical consisting of a modified gibbsite sheet where the hydroxyl of one side of a gibbsite octahedral sheet lose protons which form bond with silicon atoms located at vacant octahedral cation sites of gibbsite. Thus, three oxygen atoms and one hydroxyl present around silicon atom make up an isolated SiO_4 tetrahedron as in orthosilicates which make a planar array on the edge of a gibbsite sheet. Because of shorter bond length between silicon-oxygen bonds than aluminum-oxygen bonds sheet change into curve shape results in a tube like structure with inner and outer diameters of about 6.4 Å and 21.4 Å, respectively, and with all hydroxyls exposed at the surface.
- B. **Allophane** are considered as a group of naturally occurring hydrous aluminosilicate minerals. They are not totally amorphous but are short-range (partially) ordered. Allophane are described by the dominance of Si-O-Al bonds where most of the aluminum atoms are tetrahedrally coordinated. Unlike imogolite, the morphology of allophane varies from fine, rounded ring-shaped particles to irregular aggregates which indicates that the ring-shaped particles may be hollow spherules or polyhedrons. Despite their indefinable structure, their chemical compositions surprisingly fall down in a relatively narrow range as the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios are mostly found to be in between 1.0 and 2.0. In general, the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of allophane is higher than that of imogolite [46].

4. Characteristics of clay minerals

Clay minerals are considered as gift for human beings as they are exploring the clay minerals continuously through research as these are of very low cost, environment friendly, easily available and non – toxic. The clay minerals are so widespread that in the world, there is hardly any country where there are no deposits of one or other kind of clay minerals. In nature, clay minerals are found with certain physical and chemical characteristics due to which these clay minerals play an important role in different fields from research to industries [47]. The clay minerals are a class of rock-forming minerals having porous like sheet structure with different distances between the sheets. The combination of the electrical conductivity of the matrix material and the pore fluid is the electrical conductivity (mS/m) of the porous material. The cation exchange capacity, a number of possible charged ions by the negatively charged surface of clay materials, depends on the number of sheets and the cations located in these structures [48]. Therefore, physical and chemical properties of clay minerals depend significantly on their sheet structure, cation- and anion-exchange capacity and adsorption ability which mainly determines their importance in different applications [49].

4.1 Cation – exchange capacity

The ability of clay minerals to adsorb certain cations/anions and their retention around outside of structural unit depends on positive or negative charge deficiency in their mineral structure.

The exchange of these adsorbed ion takes place with other ions. The quantitative relationship between different reacting ions makes the exchange reaction completely different from simple sorption. Cation-exchange capacity (CEC) is the measurement of number of cations retained on the surface of soil particles [50]. It has been defined as quantity of cations that are available for exchange with other cations at a given pH and usually expressed in milliequivalent/100 gram of dry clay. Negatively charged ions present on the surface of soil particle bind with positively charged ions but allow them to exchange in the surrounding soil water with other positively charged particles results in alteration of chemistry of soil [51]. The various aspects of soil chemistry are affected by CEC. As CEC indicated the soil capacity to retain the nutrients like K^+ , NH_4^+ , Ca^{2+} , therefore, the soil fertility is measured by CEC. It also indicates the capacity to retain pollutant cations like Pb^{2+} . (CEC Wikipedia) CEC depends on particle size, crystallinity perfection and adsorbed ion therefore for a given mineral, values exist in range rather than single specific capacity. The exchange capacities also depend on pH due to the presence of hydroxyl group on the surface of certain clay minerals like allophane and kaolinite.

The original negative charge layer is either replaced or exchanged by the adsorbed cations. This ability of colloidal particles such as clay minerals to maintain and exchange positively charged ions is important because it governs the mobility of positively charged chemical species both in soils and in general geochemical cycling of cations as shown in **Figure 6** [52]. CEC is a reversible process and normally correlated with clay minerals due to the presence of interlayer exchangeable cations such as smectites. The cation-exchange capacities of the clay minerals is given in the **Table 1**.

There are various cations which do not have same replacing power and not equally replaced under a given set of conditions. For example, calcium will easily replace sodium than sodium will replace calcium. Due to similar size potassium and ammonium ions, they easily fit in the hexagonal cavities of the silicate layer. Vermiculite and vermiculitic minerals preferably and irreversibly adsorb these cations and fix them between the layers. Heavy metal ions such as copper, zinc, and lead are strongly attracted to the negatively charged sites on the surfaces of the 1:1 layer minerals, allophane and imogolite, which are caused by the dissociation of surface hydroxyls of these minerals.

The method used to determine the CEC mainly include the complete exchange of cations by a cationic species like ammonium, Na, K, Co(III) hexamine complex, Ba and Cu(II)ethylene diamine complex. The indirect method to determine CEC mainly involves the exchange of naturally occurring cationic species in clay minerals with organic cations such as alkylammonium. Depending on the method

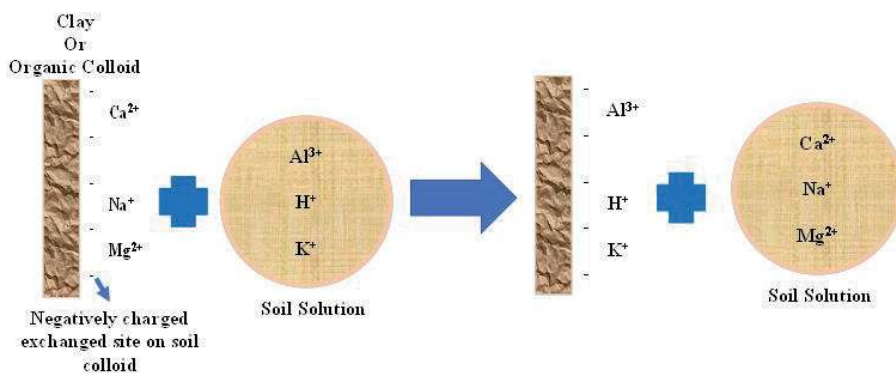


Figure 6.
Clay minerals showing the cation exchange capacity.

used for determining CEC, if the exchanged cations are present in excess, they are removed in subsequent step and the cations retained on the surface of clay are determined.

Methylene blue used for determination of CEC in a rapid qualitative procedure but when compared with other methods, results were not appropriate [53, 54]. Some other complexes like an Ag thiourea complex, Co(III) hexamine complex, and Cu(II) ethylenediamine complex [55–57]. Due to high affinity of clay minerals for these ions, CEC can be determined directly.

There are some other techniques like potentiometric titration, surface tension measurement which are used for determination of CEC. The potentiometric titration used for different types of clay minerals like Colay 90Wyoming bentonite, Na-Montmorillonite and Illite bearing shale whereas surface tension measurement used for Montmorillonite, Kaolinite and Illite [58].

4.2 Swelling capacity

If dry clay minerals are allowed to adsorbed water in a controlled environment, water is added into their interlayer space in more or less discrete forms of layer causing swelling or expansion of the interlayer space. The swelling of interlayer space of clay minerals is due to the hydration energy forces associated with the particles interaction [59]. The swelling clays are prone to large volume change which are related to change in water content. The swelling capacity of clay minerals depends on the following factors:

- The layer charge density of clay minerals
- The type of the interlayer ions whether they are monovalent or divalent.
- The concentration of ions presents in the surrounding solution with clay minerals.
- The amount of water present in the interlayer of clay minerals.
- The quantity and types of minerals i.e. composition of clay minerals

The swelling capacity phenomenon depends on granularity as well as superficial activities of clay itself. Swelling clay minerals are geological type of materials containing the mineral particles more than 50% with less than 2-micron size. The main mineral components of clay minerals are dispersed layer silicate [60]. The swelling properties of clay minerals play an important role in design of structures of light buildings. However, clay minerals/soil are heterogenous in nature; their chemical composition depends on other elements also instead of swelling minerals. There are several mineralogical research which discuss about the swelling and non – swelling clay minerals.

The mobilization of swelling capacity may result stability concerns and foundation threats, tunnels and slopes which required certain assumption and factors like swelling potential which need to be mobilized by applying the swelling pressure. The factors affecting the swelling potential are known as internal factors (cations present in clay minerals and properties of clay minerals) and factors having significant effect on swelling potential are known as external potential (properties of ions and available pore water) [61].

Swelling pressure mainly depends on the average specific surface area, more surface area, more Swelling pressure mainly depends on the average specific surface

area, more surface area, more force acting on the surface results in high volume change and high swelling pressure [62]. During the swelling process, deformation of crystal structure in clay minerals takes place results in change in mineral strength and hydraulic conductivity. The structure of clay minerals showing swelling capacity is represented by sheets of SiO_4 -tetrahedrons and $\text{Al}(\text{OH})_3$ -octahedrons which are bonded by oxygen molecules and combined to each other through interlayer having free and exchangeable cations and water molecules with variable thickness and ratio [63]. The clay minerals showing more expansion belongs to 2:1 group of clay minerals with tetrahedrons and octahedrons layers where cations and water molecules are stored in the interlayer spaces [64]. The difference between swelling and non-swelling clay minerals is the size of interlayer space. Greater the interlayer space, more change will be in swelling behavior. The interlayer spacing is measured using X-Ray Diffraction analysis. The swelling clay show more interlayer spacing while non-swelling clay show less interlayer space (**Table 2**). The mechanism of swelling of clay minerals is shown in **Figure 7**. The water molecules attached to the surface of clay minerals which is negatively charged results in hydration during the swelling process for most expandable clay minerals. The hydration is the first step in swelling process. The hydration process results in osmotic swelling where water molecules flow toward interlayer of clay minerals having high ion concentration as there is difference in concentration of ions between the unit layers and in the pore water [64].

S. N.	Clay Mineral	Type	Basal Spacing (Å)	Swelling Potential
01	Kaolinite	1:1	7-2	Almost none
02	Montmorillonite/Bentonite	2:1	9-8-20	High
03	Vermiculite	2:1	10-15	High
04	Mica	2:1	10	Low
05	Chlorite	2:1:1	14	None

Table 2.
Basal spacing of different types of clay minerals on the basis of swelling potential.

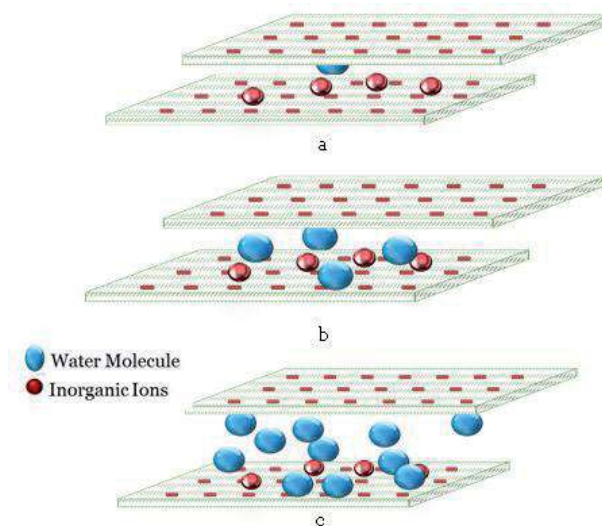


Figure 7.
(a) Non-swelling clay minerals, (b) clay minerals with low swelling capacity and (c) clay minerals with high swelling capacity.

4.3 Surface charge properties

The surface charge of clay minerals affects various chemical properties of clay minerals by varying the quantity of electrical and surface charge density. The surface charge properties play an important role in the formation of organo complexes of clay minerals, migration of ions, swelling and shrinkage. On the basis of difference in surface properties, clay minerals are categorized into two categories:

- A. Clay minerals having permanent negative charge: The permanent negative charge in clay minerals occurs due to the isomorphous substitution in the tetrahedral and octahedral layers. This type of charge is also known as structural charge and is pH independent. The negative charges of clay minerals are mainly balanced by the interlayer ions present in the interlayer space of clay minerals. The basal plane of clay minerals are permanently charged through which overall negative charge originated which is measured over pH from 2 to 12 for many clay platelets as shown in **Figure 8**. The edges faces are pH dependent results in anisotropy of clay particles [65]
- B. Clay minerals having Variable charge: The charge arises due to the protonation of Si – OH group present on the edges of clay surface. This type of charge is pH dependent. It may either be positive or negative due to the protonation or deprotonation of functional group of clay minerals depending on the pH [65, 66].

The different basal planes such as Kaolinite, gibbsite have different charging properties as the surface charge is affected by salt concentration. In case of edge surface, when hydroxyl group expose to the solution, absorbing or release of protons takes place depending on nature of hydroxyl group and proton concentration in the solution. The most important property related to charge of clay minerals is point of zero charge (pH_0) indicating the condition where the clay minerals carry positive or negative charge. According to Uehara and Gillman, pH_0 is the pH positive and negative charge varies with charge components where these are equal. The surface charge not mainly affects the aggregation of clay particles by also contaminants uptake from the electrolyte solution. The data used to describe the surface charge is collected under the ambient conditions like room temperature and pressure. The behavior of oxide minerals particle can be understood with respect to their charging properties as different crystal planes of a given particle has uniform charge properties. Various crystal faces exposed by the clay platelets show different properties to the surrounding solution results in significant anisotropy [67].

The negative charge present on clay surface is also examined by anion exclusion and cation adsorption in a region near the clay surface known as electrical double layer (EDL). The anion exclusion and electrophoretic mobility can be measured in aqueous dispersion of clay particles indicating the thickness of EDL in terms of several nanometer which completely depend on the ionic strength [68]. The EDL can be conceptually subdivided into a Stern layer containing inner- and outer-sphere surface complexes and a diffuse layer containing ions that interact with the surface through long-range electrostatics [69, 70]. The surface chemistry of clay minerals can now be described by two processes like physisorption and chemisorption of molecules and ions which takes place in the interlayer space and at the edges of the clay mineral layers. For better description of the surface properties, surface electric properties like surface potential and surface charge density are required [71, 72].

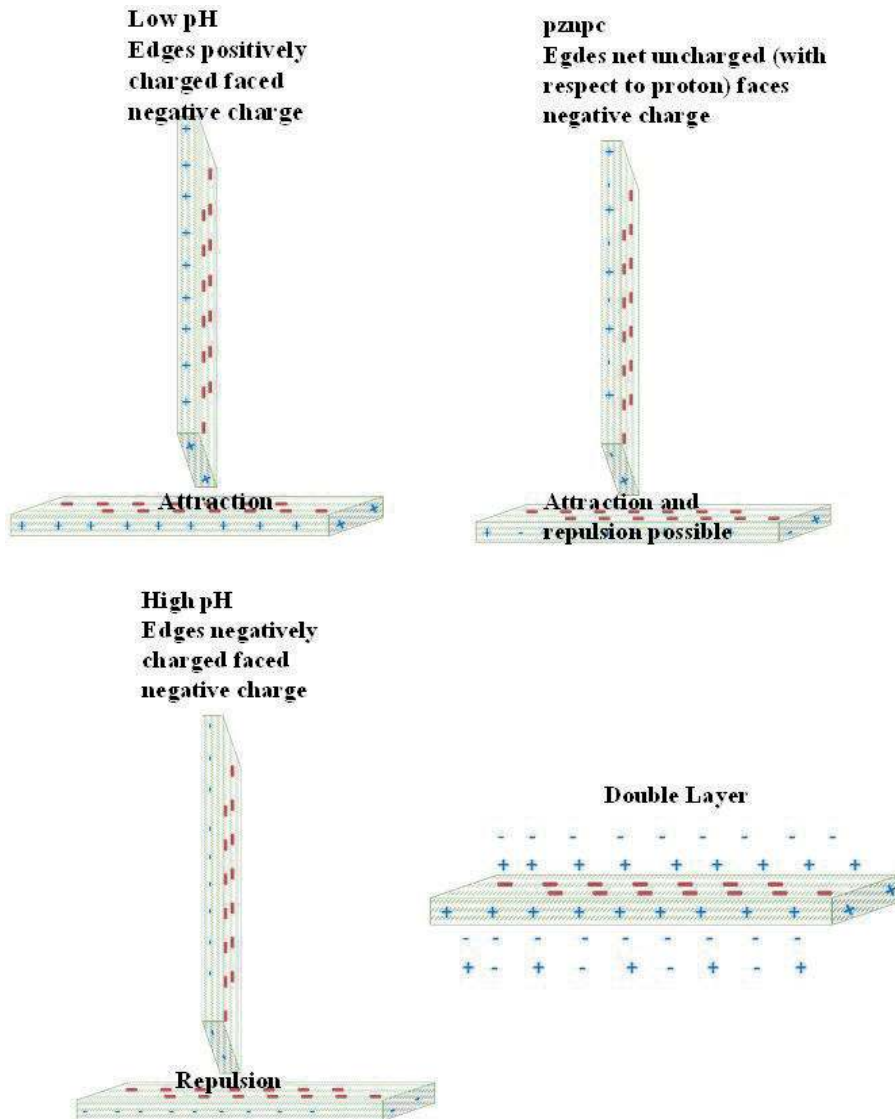


Figure 8.
Surface charge of clay minerals at different pH.

4.4 Adsorptive properties

Clay and clay-based minerals show non-covalent adsorptive behavior through three ways onto various molecules from liquid to gaseous state.

1. Physical adsorption where non-ionic adsorption takes place onto the clay surface (larger surface area compromised in small volumes).
2. Ion exchange adsorption which takes place either through the electrostatic interaction or exchange.
3. Addition of small molecules in pore/cavities and partial or complete elimination of large molecules by the cavities through zeolitic adsorption action [73].

The adsorption capacities of clay minerals depend on various factors. The high adsorption capacities of clay minerals for metal ions, organic matters and other substances are due to large surface area, low permeability, high cation exchange capacities and high retention capabilities. There are some other factors like structure and chemical composition of clay minerals which affects their adsorption capacity. There are different active sites in the clay minerals through which adsorption takes place: i) exchangeable cations (Na^+ , K^+ , Ca^{2+}); ii) hydroxyls of acidic/basic character (SiOH , $\text{SiO}(\text{H}^+)\text{Al}$, Al-OH , and OH or Mg-OH); iii) coordinatively unsaturated ions of Al^{3+} , Mg^{2+} , and/or Fe^{3+} ; and (iv) oxygen anions O^- . Such active sites present on the surface and the structural elements results in physical adsorption through Vander wall interaction of hydrogen bonding which takes place through the hydroxyl group present on the surface. Secondly, chemisorption also takes place due to the formation of chemical bond formed through stronger interaction between surface and molecules [74, 75].

4.5 Specific surface area (SSA)

Specific surface area (SSA) is defined as the surface area of soil particles per unit mass (or volume) of dry soil. Its unit is in m^2/g or m^2/m^3 . The clay minerals show high specific surface area due to the high soil water contaminant interaction results in high reactivity. The reactivity is different for different clay minerals (Kaolinite < Illite < Montmorillonite). The surface area of clay minerals mainly depends on the particle size and shape of the constituents present in clay minerals. As the particle size decreases, the specific surface area increases that can be both internal as well as external. This statement is true in case of the clay minerals which have large fraction of internal surface area such as smectite, vermiculite, sepiolite and palygorskite.

The specific surface area is different for different types of clay minerals. The expanding clay minerals like Montmorillonite and Vermiculite have high specific surface area up to $810 \text{ m}^2/\text{g}$ (combination of both internal and external surface areas) whereas non-expanding clay minerals like Kaolinite have specific surface area up to $10\text{--}70 \text{ m}^2/\text{g}$ as they show only external surface area due to non-contribution of interlayer surface as shown in **Table 3** [76]. The specific surface area can be increased by treatment of acid activation mainly with inorganic acids.

4.6 Plasticity

Plasticity of clay mineral is one of the important properties. It is the deformation of shape of clay minerals under the influence of finite force. It is defined as property of material which allow it to be repeatedly deformed without rupture

S.N.	Clay Mineral	Type	Specific surface area ($\text{m}^2 \text{g}^{-1}$)
01	Kaolinite	1:1	5–20
02	Montmorillonite/Bentonite	2:1	700–800
03	Vermiculite	2:1	500–700
04	Mica	2:1	50–200
05	Chlorite	2:1:1	—
06	Sepiolite/palygorskite	2:1	150–900

Table 3.
 Specific surface area of different types of clay minerals.

when acted upon by a force sufficient to cause deformation and which allows it to retain its shape after the applied force has been removed. The plasticity of clay minerals is affected by their composition (types of clay minerals, proportion of non-plastic minerals etc.), organic substances, specific surface area, dispersion state of particles, particle size distribution and water characteristics (viscosity and surface tension). The other factors are pressure applied, body temperature and nature of additive used. High plasticity of clay-water system require more force for deformation which occurred to a greater extent without any cracking as compared to clay-water system having low plasticity which easily deform and rupture. The plasticity of clay minerals is related to morphology of clay minerals having platelet like structure which slide over each other after addition of water content. As the water content in clay minerals is increased, plasticity also increased up to maximum depending on nature of clay. Plasticity also known as extrudability, ductility consistency or workability.

When water is added in dry clay, cohesion is increased and tend to maximum after displacing of air from the pores present between clay particles. When water reaches into the pores, formation of high yield strength body takes place results in cracking or rupturing due to the deformation. The minimum quantity of water required to make plastic clay is known as plastic limit. When the water content increases in the clay, it converts into paste where the yield strength gradually reduced. The clay become sticky to fingers. The water content corresponding to this state is known as liquid limit. With further increasing the water content, dispersed form of clay obtained. The difference in water content between these two points is expressed as plasticity index [77, 78].

4.7 Dispersion/flocculation

Dispersion is defined as a system where solid/liquid particles are dispersed into the continuous phase of liquid/solid/gas of different composition. In case of clay minerals, when they are wetted, separation of particles of clay minerals takes place results in formation of dispersion. Are detached. The flocculation is defined as when the particles such as of clay minerals dispersed into the solution, they come in contact and adhere with each other to form clusters, flocks or clumps of larger size (Figure 9). The clay dispersion is regulated by repulsive and attractive forces at the surface of charge colloid in electrical double layer. For dispersion of clay particles, there should be balanced between attractive and repulsive forces which is examined by exchangeable cations and ionic strength of the clay solution [79]. The dispersion of clay particles affected by variation in pH. Depending on oxide content and

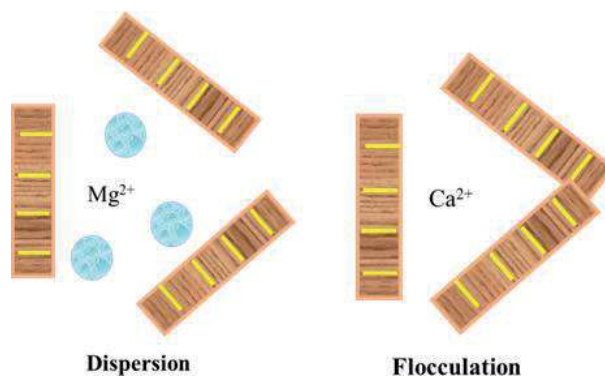


Figure 9.
Dispersion and flocculation in clay minerals.

composition of clay minerals, they exhibit net negative or positive charge at high or low pH.

Suarez et al., (1984) reported that clay dispersion increased with increasing pH at constant sodium adsorption ration and electrolyte concentration for arid-zone clays; kaolinite and smectite [80]. For example, in case of sodium saturated clay, the particle charge depends on protonation of aluminol and silanol group which are affected by pH results in alteration of dispersion/flocculation behavior of clay minerals [81, 82]. The influence of pH plays an important role during the analysis of electrokinetic properties of clay minerals. In case of electrical potential of clay minerals, the effect of pH can be related to amount of variable charge present on external surface of the particles [83].

5. Characterization of clay minerals

At present, identification and characterization of clay minerals can be done in easier way using modern analytical techniques such as Nitrogen Adsorption Isotherm, X-Ray diffraction (XRD), Fourier-Transform Infra-Red (FT-IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Zeta potential and Thermal Gravimetric Analysis (TGA). The nitrogen adsorption isotherm used for analyzing the specific surface area, pore volume and pore size distribution by characterizing the porous materials like clay minerals. XRD is mainly used for identification of crystallinity of clay minerals. The characteristic peaks clay minerals like illite, kaolinite, chlorite, smectite etc. can be identified using XRD pattern which further gives information about the interlayer space. The interlayer space is determined using Bragg's equation ($n\lambda = 2d\sin\theta$). For example, the characteristics peak of Montmorillonite is around 6.0° with interlayer spacing of 14.2\AA and when this clay mineral is treated with a surfactant/acid, the interlayer spacing will be increased. FT-IR technique is used for identification of functional group like hydroxyl group, Si-O, Al-O group etc. For example The OH stretching vibration band that manifests at 3698.1 cm^{-1} , 3622.6 cm^{-1} , 3411.7 cm^{-1} , 1638.9 cm^{-1} , 1032.2 cm^{-1} , 914.3 cm^{-1} and 799.2 cm^{-1} indicate the presence of kaolinite. Scanning electron microscopy used to study the surface topology of clay minerals such as the size of platelets and their shape mainly describes the surface morphology. SEM does not provide any information about the structure of clay minerals even after modification with surfactant or any acid. Transmission electron microscopy is used for studying microstructure and micromorphology of clay minerals by observing the stacking of layers and interlayer space [84, 85]. Zeta potential mainly used to study the surface charge of clay minerals. Zeta potential holds the information about electric double layer of charged particles whose magnitude is proportional to particle charge adhere on outer surface of clay minerals. Thermo gravimetric analysis used for determination of thermal stability of clay minerals. The curve obtained during analysis at various temperatures indicates the dehydration, dehydroxylation and phase transformation of clay minerals [86].

6. Modification of naturally occurring clay minerals

Naturally occurring clay minerals has mixed cations present on the surface and in interlayer space due to which it is impossible to use clay minerals for certain purposes as surface properties do not allow. Therefore, the interlayer space of clay minerals saturated with desired cations to confer physic-chemical properties which makes them unique for certain applications. Clay minerals are

modified to enhance the properties of clay minerals like adsorption capacity, specific surface area, permeability etc. Different ways used to modify the clay minerals like ion exchange using cationic or anionic inorganic/organic complexes, binding of inorganic/organic anions, mainly at edges, reaction with acids, pillaring by different types of poly (hydroxo metal) cations, interlamellar or intraparticle and interparticle polymerization and physical treatments such as lyophilisation, ultrasound, and plasma. Clay minerals can also be modified by pillaring using suitable pillaring agent allowing the layers of clay minerals to open results in their high resistance, high thermal stability, porosity, surface area and basal spacing [87, 88].

A well-known method of ion-exchange is to use alkylammonium ions to make the clay minerals compatible with hydrophobic material in different processes. The natural and synthetic clay minerals can be modified through exchange of interlayer cations using particular organic cations like l-carnitine, spermine, hexadimethrine, tyramine, phenyltrimethylammonium, and hexadecyltrimethylammonium results in development of new types of inorganic-organic hybrid materials. These large organic molecules intercalated in the interlayer of clay minerals results in expansion of interlayer space [89]. The modified clay minerals can be characterized using different analytical techniques like XRD, FT-IR, SEM, TEM etc. as discussed above.

The pillaring of clay minerals is done by cation exchange method where mainly inorganic molecules, hydroxyl polycations of polynuclear metals like Al, Cr, Zn, Ti etc. are introduced into the interlayer of clay minerals [90].

7. Conclusion and outlook

The abundant clay and their minerals are derived from raw materials from small to wide range of composite make them suitable for different environmental application and purposes. They are most common type of sedimentary rock and formed by weathering of these rocks at the earth's surface. They are known as 'chemical sponge' as they can hold water and other inorganic ions results in holding unbalanced charge on their surface due to which some clay minerals are positively charges and some are negatively charged. Due to the presence of water and inorganic ions, clay minerals shows remarkable characteristic which make them unique for different applications. The physico-chemical properties of clay minerals like specific surface area, ion exchange capacity, adsorption capacity, swelling capacity can be enhanced through modification with different organic cation which makes them unique for certain applications like low cost remediation of contaminated water bodies and soil.

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