Characterization and Applications of Clay as a Novel Material

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Edited by

Neeraj Kumari and Chandra Mohan

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CHAPTER 1

INTRODUCTION TO CLAY MINERALS AND THEIR CLASSIFICATION

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Abstract

"Clay is a naturally occurring material made up of fine-grained minerals that are pliable at sufficient water content and hardens when burnt or dried." Clay minerals are mostly silicates with a size of fewer than 2 microns. These are known as layer silicates that form at the earth's surface as a result of the chemical weathering of other silicate minerals. They are most common in shales and sedimentary rock. Clay minerals are fairly stable in chilly, dry, or temperate conditions and are a significant component of soil. Clays are abundant on the surface of the earth, forming shales and being a key component of practically all sedimentary rocks. Clay materials have unique qualities such as cation exchange, plastic behavior when wet, catalytic abilities, swelling behavior, and low permeabilities due to the small size of the particles and their distinctive crystal structures. Clay minerals are a type of rock-forming mineral with a porous sheet structure and varying spacing between sheets. All clay minerals have a potent attraction to water. When wet, some swell easily and even double in size.

Clay minerals are used as coatings on paper to provide whiteness and allow appropriate ink absorption, as catalysts in many industries, to purify oils, in pharmaceuticals, in the ceramic industry to build bricks, chinas,

and porcelains, and in a variety of other industries and activities. Because of their cation-exchange capacities, low permeability, and long-term structural stability, clay minerals, particularly montmorillonite, are employed as clay barriers for nuclear and chemical wastes.

Keywords: Sedimentary rocks, Clay minerals, cation exchange capacities, Sheet Structure.

Introduction

Initially, the definition of clay was given by Georgius Agricola (founder of geology) in 1546. The definition of clay has been changed a number of times, resulting in problems being raised about clay compositions (Blatt et al., 1980). The Joint Nomenclature Committees (JNCs) of the Association Internationale pour Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS) made great efforts to solve all the problems. According to the above-mentioned societies, clay is a naturally occurring substance that comprises fine-grained minerals. Clay becomes soft in water and hardens when dried. Based on this definition, clay like materials and engineered clay can be differentiated (Hiller, 1995). Clay minerals behave like “chemical sponges” when dispersed in water and can dissolve plant nutrients which have been worn out from other minerals.

The chemical composition of clay minerals is like micas, though micas contain fine-grained particles and are only visible under a microscope. The appearance of clay minerals is like flakes, with uneven edges and one smooth side, just like micas. Clay minerals are found in different shapes and sizes. Hydrous aluminosilicate minerals form soil’s clay-sized fractions. Their chemical and structural compositions are like primary minerals present in the Earth’s crust. Primary minerals are obtained from metamorphic rocks at high temperatures or pressure. Under the earth, these minerals are present in a stable form and become unstable when exposed to ambient conditions.

Clay and clay deposits: How and where do they form?

Often, clay and clay minerals are present in a small number of geologic forms like soil horizons, oceanic sediments, volcanic deposits, and weathering rocks. The formation of clay minerals occurs when rocks encounter water, air, or steam. The most common examples are sedimentation in sea or lake bottoms, weathering of rocks on hillsides, and rocks coming in contact with magma-heated water. The formation of clay minerals can also occur under any of the above-mentioned conditions. When there is any modification of rocks, clay deposits appear in pure form.

The mining of clay and clay minerals is not new – it has been continued since the Stone Age. Currently, clay minerals are one of the most significant minerals used in different fields for different purposes. The United States Geological Survey (USGS) investigated the characteristics of clay minerals and their formation. According to them, the word ‘clay’ can be used for those materials whose particle size is less than 2 micrometers with a similar chemical composition and crystal structure (Velde, 1995). Clays are prepared by the combination of fine-grained clay minerals and other minerals like carbonate, metal oxide, and quartz. Clays and clay minerals are present on/or near the Earth’s surface and produced with little environmental impact.

Mineral Structure of Clays

A crystalline element which developed due to geological changes is known as a mineral. The amplest group of minerals including clays is aluminosilicate, made up of aluminium, silicon, and oxygen counterions. They are also known as complex silicates. Based on the arrangement of these ions, there are two types of crystalline units (Figure 1.):

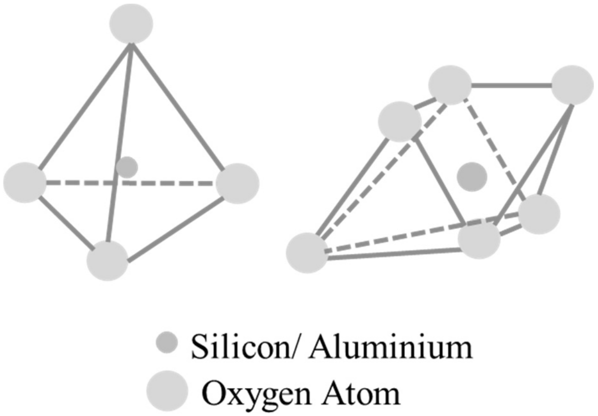

Figure 1. Tetrahedral and Octahedral Unit in Clay Minerals.

- A tetrahedron unit with silicon surrounded by four oxygen atoms which combines to form silica sheets. Silicon is the main dominating atom in a tetrahedral sheet and is present as a Si^{4+} ion. The formation of a tetrahedral sheet takes place through the sharing of three oxygen atoms. These oxygen atoms (also known as basal oxygen) link all tetrahedra in one plane and the fourth oxygen atom (known as apical oxygen) remains free and form a bond with other polyhedral elements. Apical oxygen is mainly responsible for providing a link between tetrahedral and octahedral sheets (Sun et al., 2009). This apical oxygen also provides a site to the octahedron to connect the tetrahedral sheet to octahedral sheet. Due to the isomorphic substitution of Al^{3+} in place of Si^{4+}, the negative charge is present in the tetrahedral sheet, resulting in the creation of charge deficiency. Si^{4+}, Al^{3+}, and Fe^{2+} are the common tetrahedral ions.
- Octahedron unit having aluminium/magnesium ion surrounded by six hydroxyl/oxygen units. In an octahedron, if the main dominating atom is aluminium, then a gibbsite sheet forms and if the dominating atom is magnesium, a brucite sheet forms (Barton and Karathanasis, 2002). In octahedral sites, two-thirds of sites are filled if Al^{3+} presents results in the formation of di-octahedral sheet, and all three sites are filled if Mg^{2+} present results in formation of

trioctahedral sheet. Therefore, in the di-octahedral sheet, two Al^{3+} atoms combine with six hydroxyl/oxygen ions and confirm $Al_2(OH)_6$, a unit cell formula. In the tri-octahedral sheet, three Mg^{2+} ions are combined with six hydroxyl/oxygen ions and confirm $Mg_3(OH)_6$, a unit cell formula.

Classification of Clay Minerals

Silicate clay minerals are formed by the combination of tetrahedral and octahedral sheets. Before the formation of clay minerals, primary materials were obtained from igneous or metamorphic rocks at high temperatures and pressure. The primary materials undergo some changes, resulting in the formation of secondary materials with leaf-like solid structures also known as phyllosilicates (Amonette et al., 2009). In phyllosilicate, both tetrahedral and octahedral layers are the main constituents and bound together by the sharing of oxygen atoms in different layers. Based on silicate layers and their way of arrangement, phyllosilicates are classified into different categories (Figure 2.):

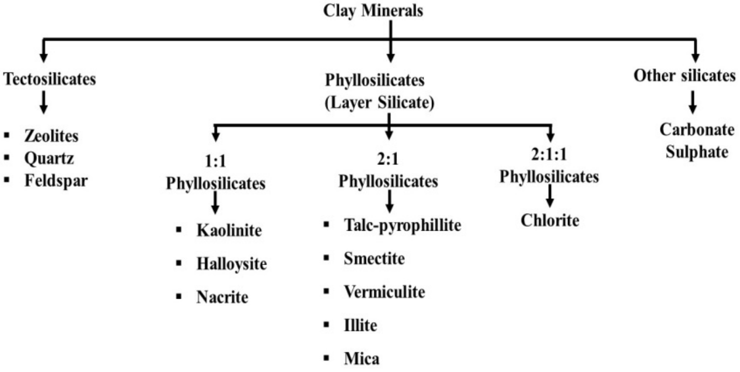

Figure 2. Classification of Clay Minerals.

Tectosilicates

Tectosilicate, also known as polysilicate/framework silicate, are significant silicate groups containing almost 75% of the Earth’s crust.

They consist of a silicate tetrahedron with a three-dimensional lattice. The oxygen atoms in the tetrahedron are linked with another tetrahedron. Therefore, it is considered that each tetrahedron is linked with four other tetrahedrons (Figure 3). Tectosilicates are negatively charged due to the isomorphous substitution of silicate by some lower charge cations like aluminium or silicates in another form.

Tectosilicates are further categorized into zeolites, quartz, and feldspar, which consist of multiple silicas, SiO_2. Zeolite and feldspar are called as aluminosilicate with $AlXSiyO_2(x + y)x$-(1:2 ratio of Si to O atoms). Feldspar is the most abundant group of rock-forming silicate including feldspar microcline and orthoclase with the chemical formula ($KAlSi_3O_8$), sanidine $(K, Na)AlSi_3O_8$.

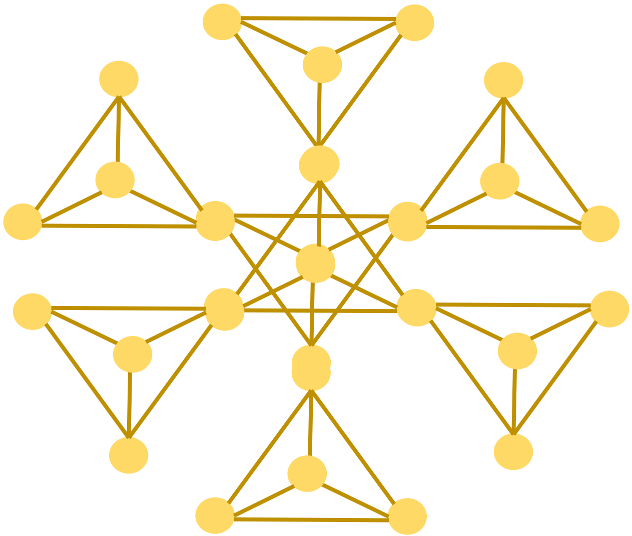

Figure 3. Tectosilicate's structure.

Axel Fredrik Cronstedt, a Swedish mineralogist, used the term 'Zeolite' in 1765 which derived from the Greek words Zeo (to boil), and Lithos (stone). In his study, he described that during the heating of a material which seems like stilbite, a large amount of heat is produced due to the water present in stilbite. When he observed such types of growth, he called this zeolite (Liebau et al., 1985). They are microporous, three-dimensional crystalline solids that have a small opening of fixed size which allows small molecules to pass through them. This small opening is called a molecular sieve. Silicon and Aluminium are the basic building unit of zeolites and are coordinated tetrahedrally (SiO_4 and AlO_4) forming an aluminosilicate framework. Zeolites are found in two forms: natural and synthetic. The common formula of zeolite is $M_{x/n}[AlO_2]_x.(SiO_2)_y.mH_2O$ where

M = metal like Mg, Na, K, Li or Ca
n = valence of metal cation
y = water molecules present in zeolite
y/x = Atomic Si/Al ratio

The metal ions are held loosely and, according to the report of December 2018, almost 253 zeolite frameworks have been known out of which 40 are naturally occurring zeolite frameworks (Augustyn, 2022).

As of December 2018, 253 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known, such as Erionite ($Na_2K_2CaMg(AlO_2)_2(SiO_2)_2.6H_2O$), Gemelinite ($Na_2Ca(AlO_2)_2(SiO_2)_4.6H_2O$) and ZSM-5 ($Hx[(AlO_2)_x(SiO_2)_{96-x}].16H_2O$).

The porous structure of zeolites can accommodate different ions like Na^+, K^+, Ca^{2+}, Mg^{2+} etc., in their cavities. These ions are held loosely and can be easily exchanged with other ions. These ion-exchanged zeolites have different acidic characters and can be used in different catalytic reactions. Zeolites are like feldspar except the size of cavities, which is larger in the case of zeolites and water (Nayak et al., 2020). Based on the structure of zeolites containing structural units, they are divided into different forms like rings or polyhedral types (Figure 4.). The diameter of cavities is between 2 - 8Å due to which ions move easily between the cavities. The reversible dehydration and cation exchange characteristics of zeolites are only due to the ease of movement of the ions and the water present in the framework. Dehydration generally depends on the way of binding water in the structure. Dehydration can occur at a higher temperature if the water is tightly bound (Rollmann et al., 1995).

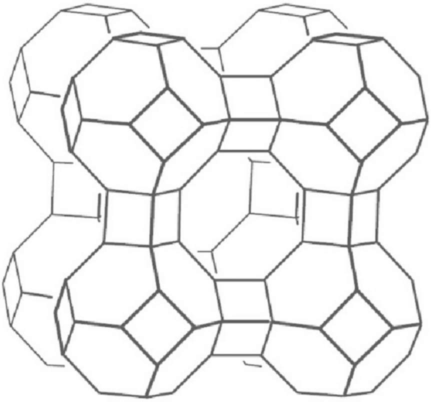

Figure 4. Structure of Zeolites.

Since the pre-historic age, quartz is one of the most popular and well-known minerals present in many geological forms in the earth's crust. The most common form of quartz is silicon dioxide or silica (SiO_2) having a hexagonal crystalline structure. It is found in igneous, metamorphic, and sedimentary rocks. Quartz is resistant to eroding in physical as well as chemical form. The concentration of grain of quartz is more in the soil, rivers, or beaches if they undergo erosion or weathering. There are two basic forms of quartz: macrocrystalline and cryptocrystalline quartz (Aggarwal, 2022).

Macrocrystalline quartz is made up of a combination of visible crystals or grains. For example, rock crystals.

Cryptocrystalline quartz, also known as microcrystalline quartz, is made up of dense and compact aggregates of microscopic quartz crystal and crystallite. For example, agate and chert.

Initially, the structure of quartz was given by Bragg and Gibbs in 1925 (Gibbs, 1926). The basic building unit of quartz is SiO_4, where four oxygen atoms are surrounded by a silicon atom and form a tetrahedral structure. As each oxygen present in the structure act as a common member for two SiO_4 groups, the formula becomes SiO_2. Due to the formation of a three-dimensional network by SiO_4 tetrahedra, quartz can be classified as a network or tectosilicate.

Phyllosilicates

Phyllosilicates are also known as sheet silicates or disilicate, where silicon is present as a central metal atom and, surrounded by four oxygen atoms at the corner of the tetrahedron. In sheet silicates, six-membered rings of SiO_4^{4-} interconnected with each other in an extended way result in the formation of infinite parallel sheets of silicate indicating a basic structural unit $Si_2O_5^{2-}$ in 2:5 ratio. These sheet silicates can be present in hydrated or non-hydrated forms, e.g., mica and talc. The phyllosilicate contains a hydroxyl group where a hydroxyl group present at the centre of six-membered rings results in the formation of $Si_2O_5(OH)^{3-}$ group (Figure 5.) (Nelson, 2015).

When a silicate sheet forms a bond with other cations, they share the apical oxygens and hydroxyl ions by coordinating with the octahedral position. A layer of ions like Fe^{2+}, Mg^{2+}, or Al^{3+} forms where octahedral coordinate with oxygen and hydroxyl ions is present in the tetrahedral sheet. Therefore, each triangle becomes the face of an octahedral group which binds to the tetrahedral layer.

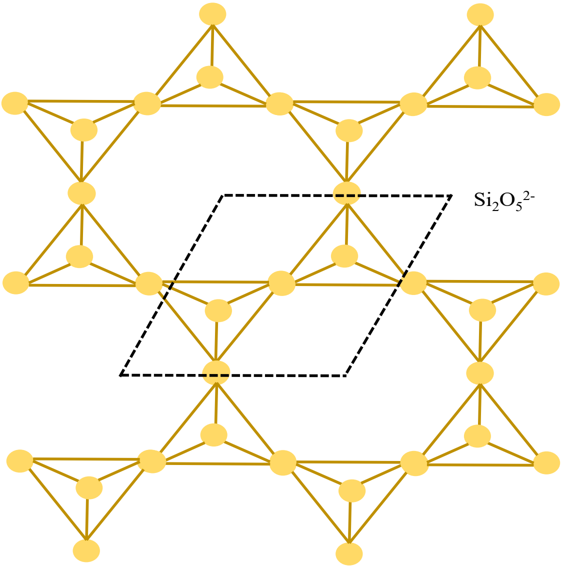

Figure 5. Arrangement of SiO_4^{4-} in form of sheet silicates.

Depending on the arrangement of the tetrahedral and octahedral layers, phyllosilicates are categorized into different categories:

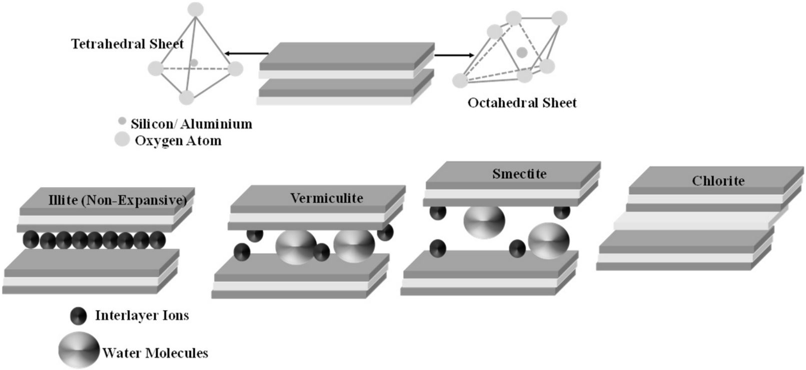

Figure 6. Classification of clay minerals depending on the arrangement of tetrahedral and octahedral sheet.

1:1 ratio of clay minerals

This type of clay mineral is formed due to weathering of feldspar. It is named after Kaolin, which is a Chinese town and is famous for the formation of porcelain. These types of clay minerals contain tetrahedral and octahedral layers as a basic structural unit, e.g. Kaolinite. In Kaolinite, one tetrahedral containing Si^{4+} and one octahedral containing Al^{3+} units are present which are joined with each other by a Van der Waal bond and a hydrogen bond through basal oxygen of the tetrahedral sheet and hydroxyl of the octahedral sheet (Varga, 2007). The general formula of Kaolinite is $Al_2Si_2O_5(OH)_4$. The hydrogen bond impedes the expansion and reactive sites of Kaolinite. There is negligible isomorphic substitution and low fertility and capacity of adsorbing cations. Kaolinite represents a dioctahedral version of 1:1 while the serpentine shows a trioctahedral version with the general formula $Mg_3Si_2O_5(OH)_4$ (Lazaro, 2015).

2:1 ratio of clay minerals

This type of clay mineral is formed due to the combination of two tetrahedral sheets and one octahedral sheet where the octahedral sheet is sandwiched between two tetrahedral sheets e.g. mica, smectite, and vermiculite. The electrically neutral 2:1 type of clay minerals is talc ($Mg_3Si_4O_{10}(OH)_2$) and Pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) where the layers are connected through Van der Waal forces. Despite the rarity of these two minerals in soils, their structure can be used to explain the trasnition that results in the creation of other 2:1 clay minerals (Uddin, 2018). The structure of talc and pyrophyllite is similar to mica except for replacement of Al^{3+} in place of Si^{4+} in every fourth tetrahedral site due to which one extra negative charge is present per formula unit. Monovalent cations like K^+, found in the interlayer sites of the 2:1 layer, satisfy the negative charge. These interlayer ions form the bond between adjacent tetrahedral layers and restrict the mineral's ability to expand. Depending on the substitution of cation in octahedral sheet and interlayer, the mica group is divided into tri and dioctahedral minerals. Phlogopite [$K\,Mg_3(AlSi_3O_{10})(OH)_2$] where Mg^{2+} is present in the octahedral sheet and Biotite where Fe^{2+} and Mg^{2+} present in octahedral sheet are the example of triocatehdral sheet while mucovite [$KAl_2(AlSi_3O_{10}(FOH)_2$] containing K^+

is present in the interlayer while Al^{3+} present in ocathedral sheet is the example of dioctaehdral sheet. Mica in the form of clay fraction shows poor crystallinity, lower concentration of K^+, high water conetnt, Fe^{2+} and Fe^{3+} substitution in octahedral sheet and Ca^{2+} in the interlayer (Yang et al, 2022). These fined grained mica also contain manganese, vanadium, lithium, chromium, titanium, and a number of other cations in different amounts.

Due to the presence of water or polar organic molecules in the interlayer space and weakly constrained cations, the 2:1 group of clay minerals shows a layer structure which is similar to mica, but the difference is in their layer charge and interlayer spacing. For example the smectite group of clay minerals, including montmorillonite and bentonite having 0.2-0.6 charge per formula unit, show an expandable dioctahedral unit. There is the isomorphous substitution of Al^{3+} in place of Si^{4+} in tetrahedral sheets and Mg^{2+} in place of Al^{3+} in octahedral sheets, which are mainly responsible for the negatively charged surface of these clay minerals. In the case of beidellite and nontronite, the tetrahedral substitution is the main source of the negative charge which is not possible in case of soil. The main difference between beeidellite and nontronite is the presence of iron in the octahedral sheet in case of nontronite. Na^+, Mg^{2+}, Ca^{2+}, and K^+ ions are present in the interlayer of 2:1 group of clay minerals along with water molecules which are mainly responsible for the expansion of the crystal lattice. When there is a saturation of water in the interlayer of clay minerals, basal spacing between the layer can expand up to 2 nm while, in case of the dry condition, it may be decreased up to 1 nm. This type of expansion and contraction often refers to swell-shrink potential and is not useful for engineers and farmers due to the formation of a crack in dry conditions resultsing instability of the surface of the soil (Bailey, 1980; Valaskova and Martynkova, 2012).

When mica undergoes weathering, interlayer K^+ is replaced with hydrated exchangeable cations due to which the formation of vermiculite takes place. In case of dioctahedral vermiculite, the main dominating ion is Al^{3+} while in case of trioctahedral vermiculite, Mg^{2+} ion is present but to a lesser extent. The isomorphic substitution of Al^{3+} in place of Si^{4+} in tetrahedral sheet takes place to a large extent as compared to smectite the group of clay minerals results in 0.6-0.9 charge per formula unit. Due to the high layer charge, the tetrahedral and octahedral layers are bound tightly with each other, and water molecules and cations present in the interlayer space are strongly adsorbed, results in the reduction of expansion of basal spacing to 1.5 nm. Unlike the smectite group of clay minerals, vermiculite shows high cation exchange capacity, especially for K^+, NH_4, and Cs^+.

Illite is dioctathedral mica-like clay mineral commonly found in sedimentary rocks. The structure of illite is similar to muscovite, as its basic unit is composed of two silica tetrahedral sheets sandwiched between the octahedral sheet. Although Si, Mg, Fe, and water are found to be more in Illite whereas less Al in the tetrahedral unit and interlayer K ions compared to muscovite (Bailey, 1980). Few interlayer ions weak the interlayer forces results in more variability in the stacking manner (Grim, 1962).

2:1:1 group of clay minerals

This type of clay mineral consists of a 2:1 basic layer structure just like the smectite group of clay minerals but one brucite or gibbsite-like sheet is also present in the interlayer, which is known as a 2:1:1 structural arrangement. The positive charge created by isomorphic substitution in the interlayer hydroxide sheet is balanced by a negative charge due to the isomorphic substitution of ions in a 2:1 layer. In brucite or gibbsite, a large number of different cations are present which results in the existence of a large number of mineral species. This type of clay mineral is non-expandable as there is no absorption of water within the interlayer – for example, chlorite (Osacky, 2015).

Chlorite is the most common sheet silicate mineral found in igneous, metamorphic, and sedimentary rocks and formed at an early stage of metamorphism. Chlorite minerals are formed under high pressure, heat, or chemical activity in clay-rich sedimentary rocks. The chlorite formed in clay-rich sedimentary rocks are associated with biotite, muscovite, and garnet (Hazen and Finger, 1978).

Other silicates

Instead of phyllosilicates, as mentioned above, some oxide, hydroxide, or hydroxy-oxide, such as sesquioxide and some poor crystalline aluminosilicates, can also be found in minute quantities in the soil clay fraction. The most common Si-oxide minerals are quartz and Al-hydroxide minerals are gibbsite [$Al(OH)_3$]. Fe containing minerals are Geothites (FeOOH). Allophane and imogolite are also an example of poor crystalline aluminosilicate clay minerals (Augustyn, 2022).

Physical and Chemical Properties of Clay Minerals

Clay minerals have various physical and chemical properties due to structural differences (such as the distribution of negative and positive charges on surfaces and the type of interactions between atoms and molecules).

Clay minerals including kaolinite, smectite, chlorite, and micas are the main components of raw clay materials that form in the presence of water. A great range of clays is used to create various structures, all depending on their mining source. They are called hydrous phyllosilicates because they contain silica, alumina, and water, as well as varying amounts of inorganic ions like Mg^{2+}, Na+, and $Ca^{2+.}$ They can be found in interlayer space or on the planet's surface. Clay minerals are distinguished by two-dimensional sheets, as well as tetrahedral (SiO_4) and octahedral (SiO_3) crystal structures (Al_2O_3).

Several clay minerals are classified based on the existence of tetrahedral and octahedral layers in their structure, such as kaolinite, smectite, and chlorite 2:1 tetrahedral and octahedral. Clay minerals have a particle size of 2 microns, which can be present in the form of plastic in the presence of water and solidify when dry. Clay minerals are remarkable in that they have a high cation exchange capacity, swelling behavior, specific surface area, adsorption capacity, and other features that are covered in this chapter due to their small size and distinctive crystal structure. Clay minerals are gaining popularity in a variety of industries due to their distinctive qualities (Kumari and Mohan, 2021).

Physical properties

1. Refractive indices and specific gravities: As the particles of clay minerals are so small, it is difficult to measure the optical properties. The refractive indices of clay minerals are found in 1.47 to 1.68 range. High refractive indices are found in the case of iron-rich minerals species, while it is less in the case of water-rich porous species. Specific gravities are found in the range of 2 - 3.3.
2. Size and shape: The size and shape of clay minerals are identified using an electron micrograph such as a Transmission Electronic Micrograph. Kaolinite is found in highly crystalline six-sided flake forms with prominent elongation on one side. Halloysite found as a tubular unit with 0.04 - 0.15 micrometer range of outside diameter. The smectite group of clay minerals shows wide undulating mosaic sheets. Sometimes small, or thin flake-shaped units can also be seen through micrographs. Illite is present in the form of poorly defined flakes which grouped and form irregular aggregates. Though, there is a large variation in the size of many clay minerals; chlorite, vermiculite, talc, and serpentine are similar in size and shape. Small spherical particles (individually or aggregated forms) with 30-50 Å diameter range are found in the case of allophane, while in the case of imogolite, thread-like tube particles are present.
3. High-temperature reactions: Destruction or modification of clay minerals depends on their composition and structure and often occurs when heated beyond dehydroxylation. Highly dehydroxylation occurs in the presence of fluxes like Fe or K. In the absence of these components, new phases may be formed by increasing the temperature just before the fusion.
4. Solubility: The solubility of clay minerals varies with acid nature, concentration, acid-to-clay ratio, temperature, treatment period, and composition of clay minerals. In acidic conditions, the solubility of clay minerals is more for ferromagnetism as compared to aluminium counterparts. The difference in the solubility may be due to the low acid concentration medium where adsorbed or interlayer ions are initially attacked by acid, followed by octahedral sheet components. When high concentration acid is used then

solubility appears consistently due to frequent occurrence of reaction. In the case of an alkaline medium, cation exchange reaction takes place followed by silica structure destruction. The most important controlling factor of the dissolution rate is the concentration of the element in an aquatic medium (Guggenheim, 1997).

Chemical Properties

1. Ion exchange: Ion exchange properties are very important in the case of clay minerals as they help to determine various physical characteristics. The positive or negative charges in the mineral structure decide the adsorption of certain ions and their retaining capacity. The adsorbed ions can be easily exchanged by other ions. The ion exchange reaction mainly shows a quantitative relationship between reacting ions, which makes it different from simple sorption. The range of cation-exchange capacity of the clay minerals is given in table 1.

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

Mineral	**Cation-exchange capacity at pH 7 (milliequivalents per 100 grams)**	**Specific surface area (square meter per gram)**
*Upper limit of estimated values.		
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*

The ion exchange capacity is found in a range instead of a specific value, as ion exchange capacity depends on particle size, crystallinity, and adsorbed ion nature. The exchange capacity also varies with pH, especially in case of imogolite, allophane, and kaolinite (as these clay minerals have hydroxyl at their surface). Different ions have different ion exchange capacities, as some ions are not replaced easily. For example, calcium ions can be easily replaced by sodium ions. The size of ammonium and potassium ion is similar; therefore, the ion can be fitted in the hexagonal cavities of the clay minerals layers.

Clay water relation

Water is present in clay minerals in various forms. Water can be present in pores which are further removed in dry conditions. In the case of the smectite group of clay minerals, vermiculite, hydrated halloysite, and sepiolite, water can be present in the interlayer position or within a structural unit. It can also be present in the interlayer space of clay minerals. Interlayer water or structural water is further divided into bound and zeolitic water. Former is attached to either exchangeable cations or the surface of clay minerals. Both forms of water can be removed by heating the clay minerals in between 100 – 200 ºC temperature and recover again at an ordinary temperature, except hydrated halloysite. The water retention capacity of clay minerals is directly proportional to their surface area. On increasing the water content, the plasticity of clay increased and changed to a near liquid state. The plasticity index and difference between the two states determine the rheological properties of clay minerals. For example, montmorillonite shows a higher plasticity index than allophane or palygorskite, indicating the prominent plastic nature of montmorillonite. Such types of rheological properties have a high impact on the foundation of building, highway construction, chemical engineering, and soil structure in agriculture practices.

Interaction with inorganic and organic compounds

The expandable clay minerals like smectite and vermiculite have many different inorganic cations between the layers. Due to multivalency ions, some large inorganic cations can be present in the interlayer space such as a hydroxy polymer of chromium, titanium, zinc, iron, and aluminium. The resulting complexes are known as pillared clays, which show high thermal stability, large surface area, high porosity, and regulated pore size. Some organic molecules like aliphatic/aromatic amines, and pyridines can also be present in the interlayer of clay minerals by replacing the exchangeable inorganic ions results in increase in basal spacing. The organic molecule present on the surface of clay minerals results in a hydrophobic character and hence lose their tendency of water binding. Subsequently, the affinity of the hydrophobic clay minerals increases for other additional molecules along with oil. Some clay minerals act as a catalyst for many reactions where one organic species transforms into another on the surface of clay minerals (Nadziakiewicza et al., 2019).

Applications of Clay Minerals

Clays have become one of the most important industrial minerals in the last few decades and they have been used in various applications with the development of nanotechnology. Clays are used to improve the quality of products and to economize on the cost to protect the environment. Clay minerals are used in various fields like a catalyst, such as in drug delivery, polymer matrix, and wastewater treatment.

Clay as catalyst

Clays are known to be a solid acid catalyst and are used in their natural and ion-exchanged form. The clay minerals can act as Bronsted and Lewis acid. Therefore, they can also act as a radical catalyst (Emam, 2013). They are used for various purposes, such as hydrocracking, reforming, alkylation, and hydrogenation due to their swelling, ion-exchange, and high specific surface area properties (Mohan and Kumari, 2022). Clays have become the most powerful tool in the petroleum refining industry. Kaolinite and montmorillonite are the most important clay minerals used as catalysts (Patel and Somani et al., 2006). The main purpose of using a clay catalyst is to make the environment pollution-free at an industrial as well as a laboratory level.

Clay as drug delivery vehicle

The basic need for using clay minerals as a drug delivery vehicle is to maximize therapeutic activities by minimizing their negative side effects. Over the past few years, clay has attracted more attention due to its layer structure, which can accommodate various polar compounds in its interlayer by forming an intercalated structure. Since the drug intercalated clay minerals release the drug in a controlled manner, these new materials have great potential as a delivery vehicle for pharmaceutical companies (Bhattcharya, 2016).

Clay as inorganic filler in polymer matrix

The addition of filler in the polymer matrix not only enhances their physico-chemical properties but also reduce the cost of the polymer. Various types of fillers such as talc and fibers are used in the polymer matrix to improve the properties of the polymer and among them, clay minerals play an important role (Mohan and Sharma et al., 2017). The addition of low amount of clay minerals in the polymer matrix has received considerable attention due to their unique functionality. Their addition leads to a significant improvement in various properties like low water absorption capacity, chemical and weather resistance power (Olad, 2011). The macroscopic homogeneity, low density, and opacity of the polymer retains even after the addition of clay minerals. The inorganic filler is also known as a reinforcement agent. When clay minerals as filler are added in the soft polymer matrix, it will carry a major portion of the applied load under stressed conditions depending on their interfacial interaction. The larger the interfacial interaction between filler and polymer, the greater the reinforcement will be. Clay minerals improved modulus and tensile strength effectively due to their rigid structure and high aspect ratio (Ramakrishna and Viraraghavan, 1997).

Clay as adsorbent

Clay minerals play an important role in environment protection as they have been used as an adsorbent for the adsorption of various hazardous materials such as heavy metals, organic dyes, oil, grease, and various other types of chemical substances and remediate the polluted water. Among natural adsorbents, clay minerals show good adsorption capacities due to their high cation exchange capacity, high specific surface area, ease of availability, and low cost. Adsorption is a major industrial separation process which has wide applicability in wastewater treatment. The adsorption capacity of clay minerals and its modified form depends on the class of dye. Since the surface of clay minerals is negative, they are good adsorbents for those heavy metals and organic dyes which are cationic in nature, as cationic dyes and metals interact with clay minerals through ion exchange/or electrostatically (Bhattcharya, 2016). Ramakrishna and Viraraghavan (1997) showed the use of bent for the removal of basic blue 9 and Thioflavin T dye from aqueous media (Jourvand and Khorramabadi et al., 2015). For anionic dyes, the surface of clay needs to modify using various cationic surfactants to convert its hydrophilic nature to hydrophobic. Jourvand et al. (2015) investigated the use of hexadecyltrimethyl ammonium bromide (HDTMA) modified Mt for the removal of methylene blue dye from aqueous media (Crini, 2006).

Clay Minerals' Negative Effects

Clay minerals, which have been approved as binders by the European Union, are commonly used in the feed industry to improve pellet quality. According to Yalcin et al., adding sepiolite to the feed of dairy cows and fattened cattle increased productivity, lowered energy consumption during pelleting, improved the pellet durability index, and reduced fine particle formation. Additionally, using bentonite in aquafeed production improved pellet physical characteristics, fish growth performance, FCR, specific growth rate, and red blood cell and hematocrit levels.

Using bentonites, zeolites, or kaolinites as pellet binders improved the quality of concentrate combinations, according to Gilani et al. Sodium bentonite boosted pellet durability and decreased the moisture and nitrogen content of broiler litter in concentration mixtures for turkeys, whereas CPL reduced litter ammonia-nitrogen levels. As a result, zeolite reduced the amount of NH_3 and CH_4 in laying henhouses. However, attaining the goal of enhancing pellet quality does not always result in a positive economic impact.

Conclusion and Prospects for the Future

Clay minerals are gaining popularity as feed additives because of their numerous benefits. Their natural origin is a significant advantage. The increased interest in the detrimental effects of mycotoxins on animals and people, along with encouraging results from recent research, appears to be a catalyst for their widespread use. Clay minerals are of special relevance in this regard because of their unique adsorption capabilities, which contribute greatly to animal health. Clays bind toxic substances and remove them from animals' bodies, allowing safe food to be produced for human consumption. Other beneficial effects of feeding clays have been observed, including antimicrobial properties, alleviation of gastrointestinal conditions through detoxification of anti-nutritional compounds in the feed, prevention of diarrheal infections, and useful properties as binding agents in the pellet manufacturing process. Clay and its minerals are numerous and are derived from a wide range of raw materials, making them appropriate for a variety of environmental applications and uses.

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