Clay minerals are important in engineering because they dominate the behavior of soils.

Clays are a specific class of minerals, hydrous alumino–silicates with a layered crystal structure.

Clay particles are also very small, colloidal in size, so their behavior is controlled by surface forces.

To understand the behavior of soil clays, it is necessary to consider both:

- the crystal structure of clay minerals and
- the surface chemistry of clay–water suspensions.
Clay minerals are made of two distinct structural units.

**Silicon tetrahedron**
- Silicon ion is tetrahedrally coordinated with four oxygen.
- \[ \text{Si} + 4 \text{O} = \text{Si}_4\text{O}_4 \]

**Aluminium Octahedron**
- Aluminium or magnesium ions is octahedrally coordinated with 6 oxygen or hydroxyls.
- \[ \text{Al} + 6 (\text{O} \text{ or } \text{OH}) = \text{Al}_6\text{O}_6 \]

Basic Units of Layer Silicates

Basic units of layer silicates are:

1. **Silica Tetrahedron**: A silicon ion is tetrahedrally coordinated with four oxygen.

   ![Silica Tetrahedron Diagram]

2. **Aluminum or Magnesium Octahedron**: An aluminium or magnesium ions is octahedrally coordinated with 6 oxygen or hydroxyls.

   ![Aluminium Octahedron Diagram]
Silicate Crystals

Clay minerals have a **layer structure**, each layer is composed of **silica and alumina** sublayers or sheets.

Silica tetrahedron is the **basic unit of layer silicates**.

A silicon is tetrahedrally coordinated with four oxygen.

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**Silicon tetrahedron**

- nm = 10^{-9} m
Silica sheets
In the silica sheet, the basic unit is the silica tetrahedron. In this unit, the silicon atom is bonded to 4 oxygen atoms.

Each tetrahedron shares 3 of its 4 oxygens to form a hexagonal structure.

This is called a tetrahedral sheet.

Tetrahedral Sheet
Several tetrahedrons joined together form a tetrahedral sheet.
Tetrahedral Sheet

In the alumina or magnesium sheet, the basic unit is the octahedron.

This unit is usually formed by aluminum or magnesium and hydroxide ions.

The aluminum or magnesium atom is bonded to 6 oxygen atoms.

Each octahedron shares all 6 oxygen atoms to form a hexagonal structure.

Octahedral Sheet

Figure 1. Structure of silica tetrahedra showing (a) a single tetrahedron, and (b) a sheet of tetrahedra arranged in a hexagonal network [1].
This is called an **octahedral sheet**.

This sheet may contain aluminum, magnesium, or both.
Octahedral Sheet

- If the cation is trivalent ($\text{Al}^{3+}$),
  \[ \text{Al}_2(\text{OH})_6 \rightarrow \text{by itself gives the mineral Gibbsite} \]
  
  \[ \text{Gibbsite sheet} \]

- If the cation is divalent ($\text{Mg}^{2+}$),
  \[ \text{Mg}_3(\text{OH})_6 \rightarrow \text{by itself gives the mineral Brucite} \]
  
  \[ \text{Brucite sheet} \]
For simplicity, let’s represent silica tetrahedral sheet by:

\[
\text{Si}
\]

and alumina octahedral sheet by:

\[
\text{Al}
\]

Clay minerals

We will combine these representations as building blocks to form the various specific clay structures in the following discussion.

These sheets combine in various ways to produce clay structures.

They combine by sharing oxygen atoms to form a chemically bonded layer.
Some minerals have layers comprised of **two sheets** (one tetrahedral and one octahedral),

while others have layers comprised of **three sheets** (one octahedral sandwiched between two tetrahedral layers).
Silicate Crystals

The different silicates are classified according to the manner in which silica terahedron associate with one another.

i. Island (independent) silicates
The tetrahedron is not joined with other tetrahedrons.

   Ex. Olivine

   Depiction of a single silicate tetrahedron.

ii. Ring and Chain Silicates

They are formed when corners of tetrahedra are shared.

   2 of the 4 oxygens are shared.

   Ex. Chains of tetrahedra: Pyroxenes

A schematic diagram of the single chain silica structure. Where two tetrahedra touch, they share an oxygen ion.
iii. Double Chain (Band)

A schematic diagram of the double chain silicate structure.

Example: Amphiboles

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iv. Sheet Structures

3 of the 4 oxygens are shared.

Example: Micas, chlorites and many of the clay minerals contain silica in a sheet structure.
V. Framework Silicates

All 4 Oxygen are shared.

Ex. Quartz \((\text{SiO}_2)_n\)
Feldspars (Orthoclase)

The structure of feldspar is similar to that of the \(\text{SiO}_2\), consisting of an infinite network of tetrahedra interconnected via bridging oxygen atoms.

In contrast to the \(\text{SiO}_2\) group, the tetrahedra may be \(\text{AlO}_4\) as well as \(\text{SiO}_4\).
Isomorphous Substitution

- substitution of \( \text{Si}^{4+} \) and \( \text{Al}^{3+} \) by other lower valence (e.g., \( \text{Mg}^{2+} \)) cations
  results in charge imbalance (net negative)

Clay Particle with Net negative Charge

- positively charged edges
- negatively charged faces
**Isomorphous Substitution**

Substitution of ions of one kind by ions of another kind with the same or different valence, but with the retention of the same crystal structure is termed “Isomorphous substitution”.

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**Isomorphic Substitution**

Isomorphic substitution is the replacement of one atom by another of similar size in a crystal lattice without disrupting or changing the crystal structure of the mineral.

**Cations** are coordinated to oxygen or hydroxyl anions in mineral structures.
The negative charge of the anions is balanced by the positive charge of the cations that are coordinated to it.

Net negative charge is developed when a cation of similar size and less positive charge substitutes for one of higher positive charge.

A negative layer charge is the result of isomorphous substitution.

Example: the substitution of $\text{Al}^{3+}$ for some of the $\text{Si}^{4+}$ in the tetrahedral sheet.

This results in a negative charge.
Mica has 25% of its Si$^{4+}$ substituted by Al$^{3+}$ in the tetrahedral sheet;

the potassium cation (K$^+$) is necessary in the interlayer spacing to neutralise the negative layer charge.

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**Negative Charge**

Al$^{3+}$ for Si$^{4+}$ in tetrahedra = negative charge

Mg$^{2+}$ for Al$^{3+}$ in octahedra = negative charge
Isomorphic substitution can also take place between:
- cations of the same charge or
- a cation of higher positive charge.

In the case of isomorphic substitution between cations of the same charge no charge is developed.

In the case of isomorphic substitution between a cation of higher positive charge with one of lower positive charge a net positive charge is developed.

The important thing to remember is that isomorphic substitution only occurs between cations of similar ionic radii.
Lyotropic Series.

Based on these principles, the relative ability of a cation to replace another (if present in equivalent quantities) is generalized by the Lyotropic Series.

\[ \text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ \]

**CATION EXCHANGE CAPACITY (CEC)**

- capacity to attract cations from the water (i.e., measure of the net negative charge of the clay particle)
- measured in meq/100g (net negative charge per 100 g of clay)
- known as exchangeable cations
- measured in milliequivalents

The replacement power is greater for higher valence and larger cations.

\[ \text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} >> \text{NH}_4^+ > \text{K}^+ > \text{H}^+ > \text{Na}^+ > \text{Li}^+ \]
Cation Exchange Capacity

The quantity of exchangable cations required to balance the charge deficiency of a clay is termed cation exchange capacity (CEC) and is usually expressed as milliequivalents per 100 grams of dry clay.
A Comparison

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Specific surface (m²/g)</th>
<th>C.E.C (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>10-20</td>
<td>3-10</td>
</tr>
<tr>
<td>Illite</td>
<td>80-100</td>
<td>20-30</td>
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<tr>
<td>Montmorillonite</td>
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<td>80-120</td>
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<tr>
<td>Chlorite</td>
<td>80</td>
<td>20-30</td>
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