Brief Introduction to Clay Chemistry

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INTRODUCTION

➢ Clays play an important part in large number of industries starting from paper, paints, cosmetics, building materials.

➢ “The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired”.

➢ Clays have a complex mineralogy and chemistry and they are essentially composed of microcrystalline particles of minerals, referred to as the clay minerals.

➢ Clay minerals are hydrous silicates containing aluminium, potassium and some other cations (Na, Mg).

➢ Industrial uses and the quality of clay largely depend on the type and proportion of clay mineral(s).

➢ Clays maybe of plastic and non-plastic minerals.
.origin of clay minerals

- “The contact of rocks and water produces clays, either at or near the surface of the earth” (from Velde, 1995).

   \[
   \text{Rock + Water} \rightarrow \text{Clay}
   \]

- For example,
  - The \( \text{CO}_2 \) gas can dissolve in water and form carbonic acid, which will become hydrogen ions \( \text{H}^+ \) and bicarbonate ions, and make water slightly acidic.
    \[
    \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-
    \]
  - The acidic water will react with the rock surfaces and tend to dissolve the \( \text{K} \) ion and silica from the feldspar. Finally, the feldspar is transformed into kaolinite.
    \[
    \text{Feldspar} + \text{hydrogen ions} + \text{water} \rightarrow \text{clay (kaolinite)} + \text{cations, dissolved} + \text{silica}
    \]
    \[
    2\text{KAlSi}_3\text{O}_8 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 4\text{SiO}_2
    \]
Clay minerals are usually ultra fine grained less than 2 μm.

Upper limit of clay size is 4 μm.
Clay in our everyday life

Pottery

Bricks

Catalytic converter

Tiles

Historical monuments
The famous terracotta artefacts and sandstone pillars of aboriginal Kacharis of Dimapur Nagaland clearly declares the intimate relationship of clay and clay products with the society for around thousand of years.
Basic Structural Units

Clay minerals are made of two distinct structural units:

**Tetrahedral Sheet**
- Connected tetrahedra, sharing oxygens.
- Tetrahedron and Tetrahedral sheets.

**Octahedral Sheet**
- Connected octahedra, sharing oxygens or hydroxyls.
- Octahedron and Octahedral Sheets.

SEM view of clay

All have layers of Si tetrahedra and layers of Al, Fe, Mg octahedra, similar to gibbsite or brucite.

All clay mineral are made of different combinations of the above two sheets: tetrahedral sheet and octahedral sheet.
Basic Unit-Silica Tetrahedra

Tetrahedral Sheet

1 Si
4 O

\((\text{Si}_2\text{O}_{10})^-\)

Replace four Oxygen with hydroxyls or combine with positive union

Several tetrahedrons joined together form a tetrahedral sheet.

- Here is a tetrahedral sheet, formed by connecting several tetrahedrons.
- Note the hexagonal holes in the sheets.

Plural: Tetrahedra

(Holtz and Kovacs, 1981)
Basic Unit-Octahedral Sheet

1. Cation
6. O or OH

Gibbsite sheet: Al\(^{3+}\)

\(\text{Al}_2(\text{OH})_6\), 2/3 cationic spaces are filled

One OH is surrounded by 2 Al:
Dioctahedral sheet

Brucite sheet: Mg\(^{2+}\)

\(\text{Mg}_3(\text{OH})_6\), all cationic spaces are filled

One OH is surrounded by 3 Mg:
Trioctahedral sheet

(Holtz and Kovacs, 1981)
Tetrahedral & Octahedral Sheets

For simplicity, let’s represent silica tetrahedral sheet by:

Si

and alumina octahedral sheet by:

Al

Silica sheet
(tips up) or (tips down)

Octahedral Sheet
(Various cations in octahedral coordination)

Gibbsite sheet
(Octahedral sheet cations are mainly aluminum)

Brucite sheet
(Octahedral sheet cations are mainly magnesium)

Mitchell, 1993
Different Clay Minerals

- All clay minerals are made of different combinations of the above two sheets: tetrahedral sheet and octahedral sheet.
- Different combinations of tetrahedral and octahedral sheets form different clay minerals:

### 1:1 phyllosilicate Clay Mineral
- Kaolinite (e.g., kaolinite, halloysite)

### 2:1 phyllosilicate Clay Mineral
- (e.g., montmorillonite, illite)

#### Clay variety depends on bonding:
- 1 sheet of SiO₄ tetrahedra — Kaolinite
- 2 sheets of tetrahedra — Montmorillonite

Usually products of alteration from original silicates
TYPES OF CLAY MINERALS

1) Silicate Clays (crystalline)
2) Sesquioxide/oxidic clays
3) Amorphous clays (non-crystalline)
1:1 phyllosilicate Minerals

$\text{Si}_4\text{Al}_4\text{O}_{10}$$\text{(OH)}_8$

Platy shape

The bonding between layers are van der Waals forces and hydrogen bonds (strong bonding).

There is no interlayer swelling

Width: 0.1~4μm

Thickness: 0.05~2μm

Hydrogen bonds in interlayer space
  - strong

Nonexpandable

Low cation exchange capacity (CEC)

Particles can grow very large (0.2 – 2 μm)

Effective surface area = 10 – 30 m²/g
  - External surface only
  - Kaolinite is used for making paper, paint, pottery and pharmaceutical industries
a) Kaolinite

Typically 70-100 layers

Joined by strong H-bond.
:. no easy separation

Layer

0.72 nm

Joined by oxygen sharing
c) Montmorillonite

- Film-like shape.
- There is extensive isomorphic substitution for silicon and aluminum by other cations, which results in charge deficiencies of clay particles.
- Always negative due to isomorphic substitution
- Layers weakly held together by weak O-O bonds or cation-O bonds
- Cations adsorbed in interlayer space
- Interlayer cations hold layers together:
  - In dry soils, bonding force is strong and hard clods form; deep cracks
  - In wet soils, water is drawn into interlayer space and clay swells.
- $n \cdot H_2O$ and cations exist between unit layers, and the basal spacing is from 9.6 Å to $\infty$ (after swelling).

- Maximum Swelling
  - The interlayer bonding is by van der Waals forces and by cations which balance charge deficiencies (weak bonding).
  - There exists interlayer swelling, which is very important to engineering practice (expansive clay).
  - High Cation Exchange Capacity (CEC)
  - High effective surface area $= 650 – 800 \text{ m}^2/\text{g}$
    - Internal surface area $>>$ external
  - Expandable........Most expandable of all clays
- Width: 1 or 2 $\mu$m
- Thickness: 10 Å .... About $\sim 1/100$ width

(Holtz and Kovacs, 1981)
c) Montmorillonite

- also called **smectite**; expands on contact with water

![Diagram of Montmorillonite structure]

- Easily separated by water
- Joined by weak van der Waal’s bond
- High affinity to water
- Swells on contact with water
- \((\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_{22} \cdot n\text{H}_2\text{O}\) structure
- A highly reactive (expansive) clay

Bentonite:
- Montmorillonite family
- Used as drilling mud, in slurry trench walls, stopping leaks
Swelling Clays

The interlayer in montmorillonite or smectites is not only hydrated, but it is also expansible; that is, the separation between individual smectite sheets varies with the amount of water present in the soil. Because of this, they are often referred to as "swelling clays".

Soils having high concentrations of smectites can undergo as much as a 30% volume change due to wetting and drying or these soils have a high shrink/swell potential and upon drying will form deep cracks.
Diagram A: Dry clay mineral

Diagram B: Expansion due to adsorption of water

Clay mineral layer

Water molecules
d) Illite

joined by $K^+$ ions

fit into the hexagonal holes in Si-sheet

Muscovite $\text{KA}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$

 Trovey, 1971
 (from Mitchell, 1993)

7.5 $\mu$m
e) Mixed Layer Clay

- Different types of clay minerals have similar structures (tetrahedral and octahedral sheets) so that interstratification of layers of different clay minerals can be observed.
- Most than one type of clay mineral is usually found in most soils. Because of the great similarity in crystal structure among the different minerals, interstratification of two or more layer types often occurs within a single particle.
- In general, the mixed layer clays are composed of interstratification of expanded water-bearing layers and non-water-bearing layers. Montmorillonite-illite is most common, and chlorite-vermiculite and chlorite-montmorillonite are often found.

![Image of Kaolinite and Illite-smectite]
Factors affecting mineral stability

- Number and type of base cations in the structure (base cations are soluble...more base cations = less stable)
  - $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, $\text{K}^+$

- Number of silica tetrahedra that are linked (more sharing of oxygens = more stable)

- $\text{Al}^{3+}$ substitute for $\text{Si}^{4+}$ (more subs = less stable)
Identifying Clay Minerals

Scanning Electron Microscope

- common technique to see clay particles
- qualitative

Clay particles are smaller than 2 microns. Their shapes can be studied by an electron microscope.
2.1 X-ray diffraction

- The distance of atomic planes {$d$} can be determined based on the Bragg’s equation.

{$BC + CD = n\lambda, \ n\lambda = 2d \cdot \sin \theta, \ d = n\lambda / 2 \ \sin \theta$}

where {$n$} is an integer and {$\lambda$} is the wavelength.

- Different clays minerals have various basal spacing (atomic planes). For example, the basing spacing of kaolinite is 7.2 Å.
2.2 Differential Thermal Analysis (DTA)

- Differential thermal analysis (DTA) consists of simultaneously heating a test sample and a thermally inert substance at constant rate (usually about 10 °C/min) to over 1000 °C and continuously measuring differences in temperature and the inert material \( \Delta T \).

- Endothermic (take up heat) or exothermic (liberate heat) reactions can take place at different heating temperatures. The mineral types can be characterized based on those signatures shown in the left figure.

For example:

Quartz changes from the \( \alpha \) to \( \beta \) form at 573 °C and an endothermic peak can be observed.

(from Mitchell, 1993)
Bentonite and other clays are used in the drilling of oil and water wells. The clays are turned into mud, which seals the walls of the boreholes, lubricates the drill head and removes drill cuttings.
Uses of Clay - Contaminant Removal

Clay slurries have effectively been used to remove a range of contaminants, including P and heavy metals, and overall water clarification.

Schematic of montmorillonite absorbing Zn
THANK YOU