1.3 CLAY MINERALS

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1.3 CLAY MINERALS

1.3.1 Composition and Structure of Clay Minerals

Clay minerals are complex silicates of aluminum, magnesium, and iron. Two basic crystalline units form the clay minerals: (1) a silicon-oxygen tetrahedron, and (2) an aluminum or magnesium octahedron. A silicon-oxygen tetrahedron unit, shown in Figure 1.9a, consists of four oxygen atoms surrounding a silicon atom. The tetrahedron units combine to form a silica sheet as shown in Figure 1.10a. Note that the three oxygen atoms located at the base of each tetrahedron are shared by neighboring tetrahedral. Each silicon atom with a positive valance of 4 is linked to four oxygen atoms with a total negative valance of 8. However, each oxygen atom at the base of the tetrahedron is liked to two silicon atoms. This leaves one negative valance charge of the top oxygen atom of each tetrahedron to be counterbalanced. Figure 1.9b shows an octahedral unit consisting of six hydroxyl units surrounding aluminum (or a magnesium) atom. The combination of the aluminum octahedral units forms a gibbsite sheet (Figure 1.10b). If the main metallic atoms in the octahedral units are magnesium, these sheets are referred to as brucite sheets. When the silica sheets are stacked over the octahedral sheets, the oxygen atom replaces the hydroxyls to satisfy their valance bonds. This is shown in Figure 1.10c.
Figure 1.9 (a) silicon-oxygen tetrahedral unit. (b) Aluminum or magnesium octahedral unit.

Figure 1.10 (a) silica sheet. (b) gibbsite sheet. (c) silica-gibbsite sheet. (I: Clay Minerals, J. Soil Mech. Found. Div., ASCE, vol 85 No. SM2 1959.)
Clay minerals with two-layer sheets. Some clay minerals consist of repeating layers of two-layer sheets. A two-layer sheet is a combination of a silica sheet with a gibbsite sheet, or a combination of a silica sheet with a brucite sheet. The sheets are about 7.2 Å thick. The repeating layers are held together by hydrogen bonding and secondary valence forces.

*Kaolinite* is the most important clay mineral belonging to this type (**Figure 1.11**). Other common clay mineral that fall into this category are *serpentine and halloysite*.

**Figure 1.11** Symbolic structure for kaolinite

- **Clay mineral with three-layer sheets**
  The most common clay mineral with three-layer sheets are *illite and montmorillonite* (**Figure 1.12**). A three-layer sheet consists of an octahedral sheet in the middle with one silica sheet at the top and one at the bottom. Repeated layers of these sheets form the clay minerals.
Illite layers are bonded together by potassium ions. The negative charge to balance the potassium ions comes from the substitution of aluminum for some silicon in the tetrahedral sheets. Substitution of this type by one element for another without changing the crystalline form is known as isomorphous substitution. Montmorillonite has a similar structure to illite. However, unlike illite there are no potassium ions present, and a large amount of water is attracted into the space between the three-sheet layers.

### 1.3.2 Specific Surface of Clay Minerals

The surface area of clay particles per unit mass is generally referred to as specific surface. The lateral dimensions of kaolinite platelets are about 1000 to 20,000 Å with thicknesses of 100 to 1000 Å. Illite particles have lateral dimensions of 1000 to 5000 Å and thickness of 50 to 500 Å. Similarly, montmorillonite particles have lateral dimensions of 1000 to 5000 Å with thickness of 10 to 50 Å. If we consider several clay samples all having the same mass, the highest surface area will be in the sample in which the particle sizes are the smallest. So it is easy to realize that the specific surface of kaolinite will be small compared to that of montmorillonite. The specific surfaces of kaolinite, illite, and montmorillonite are about 15, 90, and 800 m²/g, respectively. Table 1.6 lists the specific surfaces of some clay minerals.

### 1.3.3 Cation Exchange Capacity

Clay particles carry a net negative charge. In an ideal crystal, the positive and negative charges would be balanced. However, isomorphous substitution and broken continuity of structures result in a net negative charge at the faces of the clay particles. (There are also some positive charges at the edges of these particles.) To balance the negative charge, the clay particles attract positively charged ions from salts in their pore water. These are referred to as exchangeable ions. Some are more strongly attracted than other, and the cation ions can be arranged in a series in terms of their affinity for attraction as follows:

\[
A^{1+} > Ca^{2+} > Mg^{2+} > NH_4^+ > K^+ > H^+ > Na^+ > Li^+
\]

This series indicates that, for example, \(A^{1+}\) ions can replace \(Ca^{2+}\) ions, and \(Ca^{2+}\) ions can replace \(Na^+\) ions. The process is called cation exchange. For example,
Cat ion exchange capacity (CEC) of clay is defined as the amount of exchangeable ions, expressed in milliequivalents, per 100 g of dry clay. Cat ion exchange capacity of some clays. The laboratory procedure for determination of CEC is given is ASTM Special Technical Publication No. 479 (1970).

### 1.3.4 Nature of Water in Clay

The presence of exchangeable cat ions on the surface of clay particles was discussed in the preceding section. Some salt precipitates (cat ions in excess of the exchangeable ions and their associated anions) are also present on the surface of dry clay particles. When water is added to clay, these cat ions and anions float around the clay particles (Figure 1.13).

![Figure 1.13 Diffuse double layer.](image)

At this point, it must be pointed out that water molecules are dipolar, since the hydrogen atoms are not symmetrically arrange around the oxygen atoms (Figure 1.14a). This means that a molecule of water is like a rod with positive and negative charges at opposite ends (Figure 1.14b). There are three general mechanisms by which these dipolar water molecules, or dipoles, can be electrically attracted toward the surface of the clay particles (Figure 1.15).
a. Attraction between the negatively charged faces of clay particles and the positive ends of dipoles.

b. Attraction between cations in the double layer and the negatively charged ends of dipoles. The cations are in turn attracted by the negatively charged faces of clay particles.

c. Sharing of the hydrogen atoms in the water molecules by hydrogen bonding between the oxygen atoms in the clay particles and the oxygen atoms in the water molecules.

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**Figure 1.14** Dipolar nature of water

**Figure 1.15** Dipolar water molecules in diffuse double layer
1.3.5 Flocculation and Dispersion of Clay Particles

In addition to the repulsive force between the clay particles there is an attractive force, which is largely attributed to the Van de Waal’s force. This is a secondary bonding force that acts between all adjacent pieces of matter. The force between two flat parallel surfaces varies inversely as $1/x^3$ to $1/x^4$, which $x$ is the distance between the two surfaces. Van der Waal’s force is also dependent on the dielectric constant of the medium separating the surfaces. However, if water is the separating medium, substantial changes in the magnitude of the force will not occur with minor changes in the constitution of water.

The behavior of clay particles in a suspension can be qualitatively visualized from our understanding of the attractive and repulsive forces between the particles and with the aid of Figure 1.16. Consider a dilute suspension of clay particles in water. These colloidal clay particles will undergo Brownian movement and, during this random movement, will come close to each other at distance within the range of interparticle forces. The forces of attraction and repulsion between the clay particles vary at different rates with respect to the distance of separation. The force of repulsion decreases exponentially with distance, whereas the force of attraction decreases as the inverse third or fourth power of distance, as shown in Figure 1.16. Depending on the distance of separation, if the magnitude of the repulsive force is greater than the magnitude of the attractive force, the net result will be repulsion. The clay particles will settle individually and form a dense layer at the bottom; however, they will remain separate from their neighbors (Figure 1.17a). This is referred to as the dispersed state of the soil. On the other hand, if the net force between the particles is attraction, flocs will be formed and these flocs will settle to the bottom. This is called flocculated clay (Figure 1.17b).

![Figure 1.16 Dispersion and flocculation of clay in a suspension](image-url)
Salt flocculation and non-salt flocculation

We saw the effect of salt concentration, $n_s$, on the repulsive potential of clay particles. High salt concentration will depress the double layer of clay particles and hence the force of repulsion. We noted earlier in this section that the Van der Waal’s force largely contributes to the force of attraction between clay particles in suspension. If the clay particles are suspended in water with a high salt concentration, the flocs of the clay particles formed by dominant attractive forces will give them mostly an orientation approaching parallelism (face-to-face type). This is called a salt-type flocculation (Figure 1.18a).

Another type of force of attraction between the clay particles, which is not taken into account in colloidal theories, is that arising the electrostatic attraction of the positive charges at the edge of the particles and the negative charges at the face. In a soil-water suspension with low salt concentration, this electrostatic force attraction may produce a flocculation with an orientation approaching a perpendicular array. This is shown in Figure 1.18b and is referred to as non-salt flocculation.

Figure 1.17 (a) Dispersion and (b) flocculation of clay

Figure 1.18 (salt and (b) non-salt flocculation of clay particles. (after T. W. Lamber, Compacted Clay: Structure, Trans. ASCE, vol. 125, 1960)