

CHAPTER II

LITERATURE REVIEW

2.1 Introduction to Clay

Clay is made up of tiny crystals, many of them are so small that they can not be seen even under the highest magnification of an ordinary microscope. These crystals are mainly composed of a mineral called kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), which chemical composition is 47% silica (SiO_2), 39% alumina (Al_2O_3) and 14% water (H_2O). Besides the kaolinite mentioned above, there are a number of other clay minerals that are quite similar in their properties, but we need not consider them in any detail because they are only minor constituents of ceramic clays. The ones that are of interest to us are montmorillonite and halloysite, which are even finer than kaolinite and are sometimes used in small quantities to enhance the working properties of other ceramic materials.

2.1.1 Structure of the clay minerals

There are two main groups of clay minerals: the kaolins and the smectites. The kaolin has the empirical formula, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, and that of the smectite has the formula, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot (10)$. We will explain only the kaolin structure, since it is the principal constituent of china clay, ball clay, fireclays, and many terra cotta clays.

The kaolin group includes the clay minerals, nacrite, dickite, kaolinite and halloysite. Their structures have one thing in common—they are composed of silica sheets linked to modified gibbsite sheets. Imagine a gibbsite sheet (Fig. 2.1 (b)) placed directly over a silica sheet (Fig. 2.1 (a)), in such a way that one in three of the OH groups is removed and replaced by the unsaturated 'vertical' oxygens of silica sheet. These latter oxygens now form a 'bridge' between the two sheets, forming a composite unit layer of kaolin type. If we write the modified gibbsite layer as $[\text{Al}_2(\text{OH})_4]^{2+}$ (i.e. having removed two OH groups) and the silica sheet as $(\text{Si}_2\text{O}_5)^{2-}$, we arrive at the composite formula $\text{Si}_2\text{O}_5 \cdot \text{Al}_2(\text{OH})_4$, or $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, the unit formula of the kaolin group.

The silica layer is often referred to as the tetrahedral layer, because of the tetrahedral shape of the SiO_4 groups. The co-ordination number of the Si with respect to oxygen, which is four, is denoted by a Roman numeral immediately above the

element thus: Si^{IV} . In the gibbsite layer, the oxygens are arranged to form the corners of octahedra, which are geometrical figures having eight faces and six corners. The coordination number of Al is thus six and represented as Al^{VI} . An important feature of the octahedral layer in the kaolinite is that only two out of three possible sites are occupied by aluminium ions, the remainder being vacant; such structures are therefore called dioctahedral. There are three possible ways of filling three sites by two ions, thus giving rise to one source of variation in the unit layers.

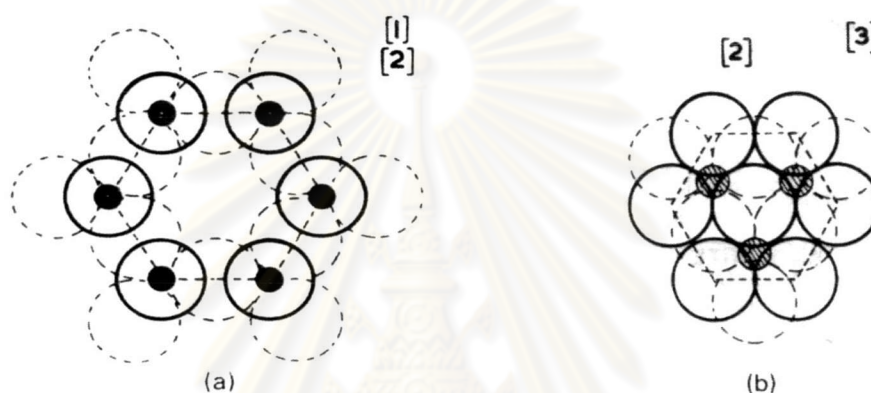


Fig. 2.1 (a) A silica sheet; (b) The gibbsite sheet.(10)

A crystal of kaolin minerals does not consist of one composite layer but of a very large number of such layers, which is likened to a book, where each page represents a single layer (Fig. 2.2). Note that there is no ionic bonding between neighboring units. The whole crystal is held together by hydrogen bond, acting between OH groups of the gibbsite layers and oxygen atoms of the adjacent silica layers. For this relatively weak secondary bonding to be effective, the appropriate oxygens and OH groups must be close together. There are several ways in which one unit can be 'stacked' upon another to achieve this bonding and this gives rise to four distinct minerals of kaolin type, viz. nacrite, dickite, kaolinite and hollloysite.

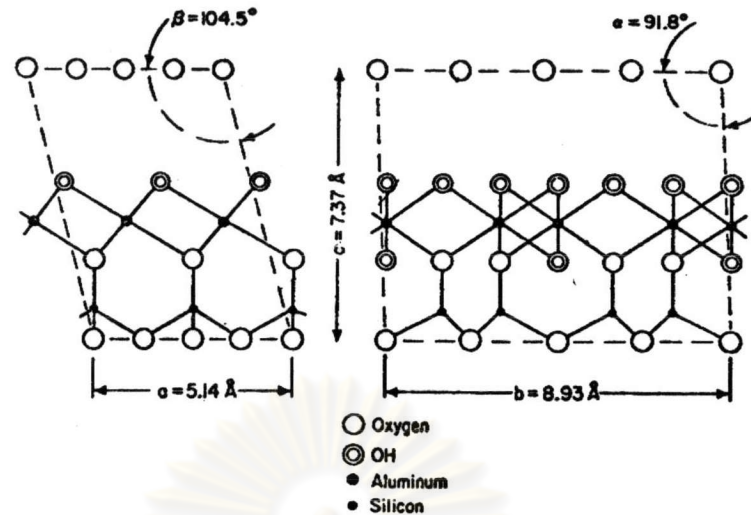


Fig. 2.2 Unit cell of the kaolinite(11)

2.1.2 Physical properties of clay minerals

(a) Particle size and shape

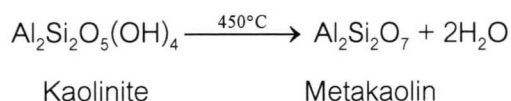
Nacrite, dickite and kaolinite exist only as very small, hexagonally-shaped platy crystals, varying from less than 0.1 μm to 2 μm in diameter, although occasionally larger crystals of up to 20 μm in diameter are found. Because they are so small, they are only observed under the electron microscope. Halloysite is a tube-shaped particle. These ultimate particles are quite hard and are not readily broken down by mechanical means. A grain is a loose agglomerate of particles, caked together, that break up when they are mixed with water and agitated. Thus although grains of dry-ground fireclay may not just pass a 240-mesh standard sieve (72 μm aperture), the ultimate particles are much smaller as can be shown by dispersing the clay in water and measuring the distribution of its particle sizes

(b) Specific gravity

The specific gravity of the clays is about 2.6. It is difficult to measure the specific gravity of montmorillonite because it swells, but the value is calculated to be close to that of the kaolins.

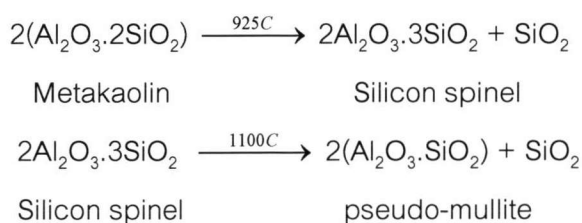
(c) Effect of heat on the clay minerals

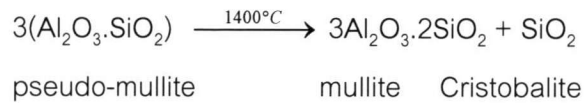
Most hydrated minerals lose water when they are heated. When kaolinite, nacrite or dickite are heated above 450 °C, they lose the water in their structure.



Even after the water has been driven off, the residue still retains some of the crystalline features of the original kaolin mineral, and is therefore called "metakaolin". Chemically, however, it behaves as if it was simply a mixture of finely divided silica and alumina. Heating clay minerals to higher temperature, the metakaolin undergoes further reaction to form crystalline compounds, the end-products being free silica (cristobalite) and mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Thus, it is clear that there occurs a separation into an alumina-rich compound and free silica, but the precise manner in which this takes place is still a matter of controversy. Earlier work, based chiefly on X-ray diffraction, indicated that at 1000°C a spinel-type compound was formed, thought to be $\gamma\text{-Al}_2\text{O}_3$. At this temperature, thermal analysis shows an exothermic peak, also thought to be associated with recrystallization of $\gamma\text{-Al}_2\text{O}_3$. Other authorities, however, attributed this exothermic peak to the formation of mullite; but this now seems unlikely, since recent X-ray work strongly suggests that mullite is not formed until much higher temperatures are attained (1150-1300 °C).

More recent accurate measurements of the unit cell dimensions of the spinel compound have shown that it is probably not $\gamma\text{-Al}_2\text{O}_3$ but a silicon-aluminium spinel, of formula $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$. This latter compound is then said to lose silica by a progressive diffusion of Si ions from the lattice forming a mullite-like compound, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, as an intermediate stage and by further loss of silica. True mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, is formed. The entire process may therefore be represented by the following chemical equations: (10)





All clays, on being heated to a higher temperature, begin to fuse and form a viscous liquid which consists principally of the excess silica, together with various impurities such as Na_2O , K_2O , CaO and MgO . These oxides lower the melting point of silica and form liquid at the comparatively low temperature of 1200°C . Therefore, these impurities are called fluxing oxides.

During firing, the liquid formed fills up pore space in the clay. Consequently, the overall volume decreases as a result of the clay body shrink. Clearly the porosity decreases also and this reduction of porosity through the formation of liquid during firing is known as vitrification

On cooling, the liquid produced does not crystallize completely, but mostly solidifies to form glass.

(d) Plasticity of clay

Plasticity of clay is defined as the ability of a clay-water mass at its maximum consistency to be shaped and to hold its shape after the forming forces are removed. (12) The word ability in this definition has two connotations, one with respect to shaping and the other to holding the shape. In the first case "ability" refers to the amount of plastic or viscous flow (strain) that can take place before rupture occurs. In the second "ability" refers to the internal strength of the plastic mass after the forming stresses are removed. This dual relation in the definition qualitatively means that a clay will have high plasticity when a large force is required to deform it, and in this condition it will be deformed to a considerable degree before failure. As a matter of fact, a clay-water system of high plasticity requires large force to deform it and deforms to a greater extent without cracking than low plasticity one which deforms more easily and ruptures sooner.

There are many factors affecting the plasticity of clay bodies, and these factors should be well understood in order to manipulate this property. Some of the factors are primary and others are secondary. The primary factors are essential to achieve

plasticity, while the secondary factors are used to control or regulate plasticity. The primary factors are:

(1) The anisodimensional shape of clay-mineral particle.

(2) The strong surface forces on clay-mineral particles due to the in completely coordinated small cations with large charge.

(3) The rigidity of the water structure surrounding the clay mineral particles.

The secondary factors affecting plasticity do not create or destroy plasticity of clay bodies but only increase or decrease its magnitude. These secondary factors are:

(1) The type of cations absorbed on the clay mineral particles and/or contained in their water hulls.

(2) The temperature of the clay-water system.

(3) The small particle size of the clay-mineral particles.

(4) The presence of nonclay particles in the clay-containing body.

(e) Drying of clay bodies

The drying of clay products is complicated and can be deduced from the long list of factors that affect the process. Some of the factors relate to those already of concern in the forming operations, and others are derived from the application of energy for water removal. All of the factors listed below contribute to shrinkage and the cost of drying, both of which must be controlled for a successful operation:(12)

(1) The initial water content affects directly on the magnitude of shrinkage and the cost of removal.

(2) Particle size of the clay minerals determines the potential for shrinkage and the amount of water required for forming, and it affects the drying rate.

(3) The amount of nonplastics in the mineralogical composition and their particle sizes affect shrinkage and drying rate.

(4) The temperature of drying is related to the rate of water removal and the final equilibrium moisture content of the ware. The application of heat to a damp clay body sets up moisture gradients within the piece that becomes part of the drying mechanism.

(5) The partial pressure of water vapor in the drying environment is one factor influencing the drying rate as well as temperature. In industrial practice the partial

pressures are monitored by measuring relative humidity. Relative humidity is defined as the ratio of present water content to the saturated water content in air at each particular temperature. Therefore, if temperature rises without adding water, relative humidity decreases.

(6) The velocity of air affects the rate of drying by controlling moisture gradients near the drying surface. This effect is operative up to some optimum velocity.

2.1.3 Chemical composition of clay

Chemical analysis of a clay tells us something about what we can expect when it is used in a body, particularly how it will behave on firing. For example, highly pure kaolins are very refractory and can not be fired to a dense structure in the pottery kiln. On the other hand, stoneware clays, which contain potash and lime, can be fired quite readily. Amount of iron oxide present in the clay tells us what the fired color will be. Composition of typical clays is shown in Table 2.1.

Table 2.1 Some examples of chemical compositions (wt%) of typical clays. (13)

| Constituent | English china clay | Ky. Ball clay | N.J. stoneware clay | Red brick clay |
|--|--------------------|---------------|---------------------|----------------|
| Silica (SiO ₂) | 48 | 53 | 68 | 57 |
| Alumina (Al ₂ O ₃) | 38 | 29 | 22 | 19 |
| Iron oxide (Fe ₂ O ₃) | 0.5 | 2 | 1.6 | 7 |
| Magnesia (MgO) | - | 0.3 | 0.2 | 3 |
| Lime (CaO) | - | 0.4 | 0.3 | 4 |
| Titania (TiO ₂) | - | 0.8 | - | 1 |
| Alkalies (K, NaO) | 2 | 2 | 2.5 | 5 |
| Combined water | 12 | 12 | 6 | 4 |
| Basic oxides | 2.5 | 4.7 | 4.6 | 19 |
| Neutral oxides | 38 | 29 | 22 | 19 |
| Acid oxides | 48 | 53.8 | 68 | 58 |

2.1.4 Earthenware clay or terra cotta clay

Most of the usable clay found in nature might be the "earthenware" clay or common clay. These clays contain iron and other mineral impurities in sufficient quantity to cause the clay tight and hard-fired at about 950°C to 1100°C . Before firing, the colors of such clays are red, brown, greenish, or gray, as a result of the presence of iron oxide. After firing, the clay may vary in color from pink to buff to tan, red, brown, or black, depending on the composition of clay and firing condition. Most of the pottery in all over the world has been made of earthenware clay, and it is also the common raw material for brick, tile, drain tile, roof tile, and other heavy clay products. Common red clay is highly plastic, in fact, too plastic and too sticky to be used by itself. On the other hand, it can be changed to nonplastic with the presence of sand or other rocky fragments. Therefore the potter will look for smooth plastic earthenware clay that can be modified by the addition some amount of sand or nonplastic clay. The brickmaker will look for an earthenware clay that is naturally coarse and contains considerable sand or other nonplastic fragments and with such a clay he will be able to press, dry, and fire his bricks without having them warp, crack, or shrink excessively.

2.2 Literature Survey on the application of Rice Husk Ash

Rice husk ash (RHA) is a by-product from power plant. The burning of rice husk in air always leads to the formation of silica ash, which its color varies from gray to black depending on inorganic impurities and unburned carbon amounts.(7) The main composition of RHA is silica, therefore, there are many applications incorporating material, as follows:

M. A. Rahman(14) investigated about the properties of clay-sand-rice husk ash mixed bricks. **Bricks were made from clay-sand mixes with different percentages of rice husk ash and burnt in a furnace for different firing times. The firing durations at 1000°C were 2 4 and 6 hours.** Test results indicated that lightweight bricks could be manufactured with rice husk ash without any deterioration in the quality of bricks. Further, the compressive strength of the bricks was higher with rice husk ash contents. The optimum firing

duration was found to be 4 hours at 1000°C. It is shown that bricks made of clay-sand-rice husk ash mixes can be used in load bearing walls.

M. R. Yogananda and K. S. Jagadishi (15) investigated the pozzolanic properties of rice husk ash, burnt clay and red mud. Compressive strength of lime-pozzolana mortars with rice husk ash, burnt clay and red mud were studied. Influence of grinding of rice husk ash and grinding with lime were also investigated. Combination of pozzolana with partial replacement of burnt clay and red mud by rice husk ash were examined. Long term strength behavior of lime-pozzolana mortars was investigated to understand the durability of lime-pozzolana cements.

V.I.E. Ajiwe et al.(5) investigated a preliminary study on the manufacture of cement from rice husk ash. Cement was successfully produced from rice husk ash. The developed cement slab, commercial cement and slab were tested for their physical characteristics and chemical composition. The tests confirmed that developed cement was of similar standard to commercial cement. Based on the results, the production of cement from rice husk was recommended for developing countries since it reduce problems of farm wastes.

I.K. Cisse and M. Laquerbe (16) investigated the mechanical characterization of sandcretes with rice husk ash additions study applied to Senegal. The mechanical resistance of sandcrete blocks obtained when unground ash (and notably the ground ash) was added revealed that there was an increase in performance over the classic mortar blocks. In addition, the use of unground rice husk ash enabled production of a lightweight sandcrete with insulating properties, at a reduced cost .The reactivity of ash with pozzolanic explained the high strengths obtained.

Veera Amnouyorn (17) investigated the influence of rice husk ash on mechanical properties of clay brick. The objective of his work was to study the effect of RHA on the mechanical properties and durability of clay brick. The ground and unground RHA were mixed with mixture of sand and clay, and bricks were produced. The percentages of RHA were 0%, 0.3%, 3% and 5% by weight. The results showed that brick mixed with 3% RHA by weight exhibited the highest value of density, modulus of rupture and compressive strength.

C.S. Prasad et al.(8) investigated the effect of rice husk ash in whiteware compositions. It had been found that the complete replacement of quartz by RHA drastically reduced both the maturing temperature and the percentage of thermal expansion, and increased the strength marginally. The improvement was attributed to sharp changes in the microstructural features as a result of significant reduction in the content of quartz phase and the simultaneous increase in glassy phase.

C.S. Prasad et al.(9) continued investigation about the effect of substitution of quartz by rice husk ash and silica fume on the properties of whiteware compositions. Active silica from RHA and silica fume (SF) were progressively incorporated in a whiteware composition in substitution of quartz. It had been found that replacement of quartz by RHA+ SF (1:1) reduced drastically both the soaking temperature (50–100 °C) and the thermal expansion (3.24–14.6%) at 600 °C as well as the improvement in the fired strength. Maximum increment of MOR (20.8%) was observed for the whiteware composition containing 10% (RHA+silica fume). On complete replacement of quartz (25%) by RHA+SF, the fired strength increased around 14.95% in whiteware body when it was sintered at lower temperature by 100°C.