6- Silicate Ceramics-a Kaolinite and Clays

Kaolinite

Kaolinite, $Si_2Al_2O_5(OH)_4$ or $Al_2O_3,2SiO_2,2H_2O$, is the most common among the argillaceous minerals used in ceramics. A projection of its crystalline structure is represented in Figure 4. It consists of an alternate stacking of $[Si_2O_5]^{2-}$ and $[Al_2(OH)_4]^{2+}$ layers, which responsible for the lamellate character that lead to the development of plates. The degree of crystallinity of the kaolinite present in clays is highly variable. It depends largely on the conditions of formation and the content of impurities introduced into the crystalline lattice.

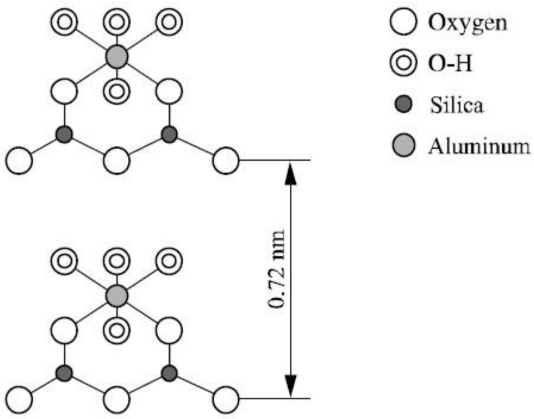

Figure 1:
Projected representation of the structure of kaolinite

Clays *(the kaolinite can be one type or component of clays)*

1- Common characteristics

i. Clays are hydrated aluminosilicate minerals whose structure is made up of a stacking of two types of layers containing, respectively, aluminum in an octahedral environment and silicon in tetrahedral coordination.

ii. The large surface area of clays (10–100 m^2g^{-1}), their plate-like structure, and the physicochemical nature of their surface enable clays to form, with water, colloidal suspensions and plastic pastes.

This characteristic is largely used during the manufacture of silicate ceramics because it makes it possible to prepare homogenous and stable suspensions, suitable for casting, pastes easy to manipulate, and green parts with good mechanical strength.

By extension, the term clay is often used to denote all raw materials with proven plastic properties containing at least one argillaceous mineral. The impurities present in these natural products contribute to a large extent to the coloring of the product.

2- Classification

The clays are not all the same towards easy manipulation and behavior during firing. Ceramists distinguish vitrifying plastic clays, refractory plastic clays, refractory clays, and red clays.

Vitrifying plastic clays

They are generally colored, are used for the remarkable plasticity of their paste. They are made up of very fine clay particles, organic matter, iron and titanium oxides, illite (formula $Si_{4x}Al_x)(Al,Fe)_2O_{10}(OH)2K_x(H_2O)_n)$ and micaceous (from mica) and/or feldspathic impurities.

These clays are also characterized by high free silica content. Sand can represent up to 35% of the dry matter weight. The product called "ball clay" is widely used for its plasticity and its particularly low mica content.

Although it contains the same argillaceous mineral as kaolin, this clay has much higher plasticity because of the much smaller size of the kaolinite particles.

Refractory plastic clays

They are rich in montmorillonite (formula $(Si4_{-x}Al_x)(Al_{x-v}R_x)O_{10}(OH)_2M_{2v}(H_2O)_n$ with R = Mg, Fe^{2+} and M = K, Na), kaolinite or halloysite ($Si_2Al_2O_5(OH)_4(H_2O)_2$).

Refractory clays

They are used in high temperature processes.

Their composition is rich in alumina. Kaolins are the most refractory among these clays. Always purified, they contain little quartz, generally less than 2% alkaline oxides in combined form, and a small quantity of mica.

Their plasticity is due to the kaolinite and, if necessary, a little smectite or halloysite.

Very low in coloring element, they are particularly suited for the preparation of products in white color.

Red clays

They are used for the manufacture of terra cotta products.

They have complex composition of actually natural mixtures.

They generally contain kaolinite, illite and/or other clays rich in alkaline, sand, mica (formula $Si_3Al_3O_{10}(OH)_2$), goethite (FeO(OH)) and/or hematite (Fe_2O_3), organic matter and, very often, calcium compounds. The latter, just like the micas and the other alkaline-rich compounds that help lower the firing temperature of the product.

7- Silicate Ceramics-

b: Feldspars and Silica

The Role of Oxides in Firing of Traditional Ceramics

Acidic Oxides: They are backbone of the ceramic and mainly improve the mechanical properties.

Formula: MO_2, e.g. SiO_2, GeO_2, TiO_2, ZrO_2, CrO_2 … etc

Basic Oxides: They are Fluxes, i.e. reducing firing temperature.

Formula: MO and M_2O, e.g. CaO, MgO, Na_2O, K_2O, Li_2O … etc

Amphoteric Oxides: They form bridges between acidic and basic oxides and partially substitute them.

Formula: M_2O_3 and M_2O_5, e.g. Al_2O_3, B_2O_3, P_2O_5 … etc

Feldspars

Four feldspathic minerals are likely to enter the composition of silicate ceramic pastes. They are:

− orthoclase, a mineral rich in potassium with the composition $K_2O.Al_2O_3.6SiO_2$

− albite, a mineral rich in sodium with the composition $Na_2O.Al_2O_3.6SiO_2$

− anorthite, a mineral rich in calcium with the composition $CaO.Al_2O_3.2SiO_2$

− petalite, a mineral rich in lithium with the composition $Li_2O.Al_2O_3.8SiO_2$

− soda Na_2O, sodash

− potash

− lucite

Orthoclase and albite, which form eutectics with silica at 990 and 1,050°C respectively, are widely used as flux. Anorthite is rather regarded as a substitute to chalk ($CaCO_3$). There is a limited use of petalite. It is used mainly to improve brightness and its negative CTE.

Potassic feldspar is particularly appreciated by ceramists because its reaction with silica leads to the formation of a liquid whose relatively high viscosity decreases slightly when the temperature increases. This behavior is considered as a guarantee against the excessive deformation of the pieces during the heat treatment.

Silica

Silica, SiO_2, is a polymorphic raw material found in nature in an amorphous (opal, pebbles) or crystallized form (quartz, cristobalite and tridymite). Sand contains between 95 and 100% of quartz mass. It is the most frequently used in the ceramic industry to contribute to the mechanical strength of the parts. In the manufacturing processes of stonewares and porcelains, it is usual to use relatively fine sand grains (20 to 60 μm).

When a ceramic is fired, the sand can react, particularly with the fluxes. This reaction is not often complete. The transformation of residual quartz into cristobalite can then start from 1200°C onwards. This transformation is enhanced by the rise in temperature, the use of fine-grained sand, the presence of certain impurities, and the use of reducing atmosphere.

The form of silica determines the thermal properties of silicate ceramics. For example, quartz and cristobalite do not have the same influence on the expansion of the product. Quartz can also cause a deterioration of the mechanical properties of the finished product owing to the abrupt variation in dimensions ($\Delta L/L \cong -0.35\%$) associated, at 573°C, with the reversible transformation β quartz → α quartz. As the crystal of cristobalite formed from the flux are usually small, the transition β cristobalite → α cristobalite, which occurs at about 220°C often causes less damage to the finished product.