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Raw materials for ceramic Industries

2.1 Introduction

Generally speaking, traditional ceramic industries use three main types of raw materials:

- **Clays** which give the main body of the product and ensure enough plasticity for the body to be shaped.
- **Feldspars** which represent fluxing components since they melt at relatively low temperatures.
- **Silica** which is the main glass forming raw material.

In addition, other raw materials are often used, including limestone, magnesite ($MgCO_3$), soda ash (Na_2CO_3), bauxite ($Al_2O_3.xH_2O$), borax ($Na_2B_4O_7.10H_2O$) etc. …

A recurrent problem when dealing with ceramic raw materials in general is that their composition is rarely kept constant over long periods of time even if they are quarried from the same location. That is why it is important to have the following properties monitored so as to ensure that the final product abides by the standard requirements in a continuous way:

Chemical and mineralogical composition – Particle size distribution – Plasticity for clays and kaolin – Drying shrinkage for clays and kaolin – water absorption - color, etc.

2.2 Plastic raw materials

These may constitute more than 50% of the composition of ceramic bodies and are necessary for the formation of the main body of the product. Besides, they impart workability to the plastic mix formed by adding other materials such as feldspars and quartz. They are usually related to the mineral kaolinite of chemical composition $Al_2O_3.2SiO_2.2H_2O$ and to a lesser extent to the mineral pyrophyllite of chemical composition $Al_2O_3.4SiO_2.H_2O$.

2.2.1 Structure of clay minerals

Both aforementioned minerals possess a sheet structure where Si – O tetrahedral and Al – O – OH octahedral are the main building units. Actually, both are characterized by the presence of a Si_2O_5 unit characteristic of sheet structures; the formulas of kaolinite and pyrophyllite minerals can be written as $Al_2Si_2O_5(OH)_4$ and $Al_2Si_4O_{10}(OH)_2$ respectively.

Kaolinite mineral possesses a sheet structure in which the unit cell consists of one Si – O and one Al – O – OH layers (Figure 2.1). That is why it is sometimes called a two layered type of clay. Adjacent groups of Si – O and Al – O – OH in adjacent sheets are bonded by moderately strong hydrogen bonds. That is why; water molecules insert themselves between the sheets with relative difficulty, which accounts for the limited plasticity of kaolinite based clays. Figure (2.2) details kaolinite structure.

Si – O Al – O – OH
Si – O Al – O – OH
Si – O Al – O – OH

Fig 2.1 Three Unit cells of kaolinite

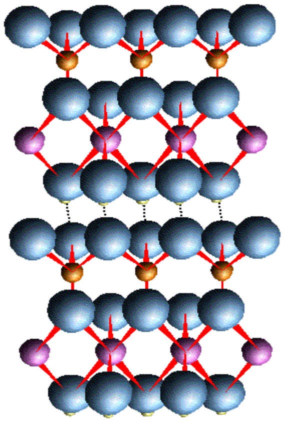

Fig 2.2 Two unit cells of kaolinite

On the other hand, pyrophyllite possesses a three layered structure where Al – O – OH octahedra are sandwiched between two layers of Si – O tetrahedra. This results in the absence of hydrogen bonds between adjacent unit cells. The only bonds between these unit cells will be of the weak Van Der Waal type. This allows for much more water molecules to insert themselves between the sheets causing swelling of the clay – water mix. Clay ores constituted out of that mineral are highly expandable and are added in small amounts in conventional ceramic mixes to enhance plasticity, a typical example being bentonite. Figures (2.3) and (2.4) illustrate the structure of this three layered mineral.

Si – O Al – O – OH Si – O
Si – O Al – O – OH Si – O

Fig 2.3 Two Unit cells of pyrophyllite

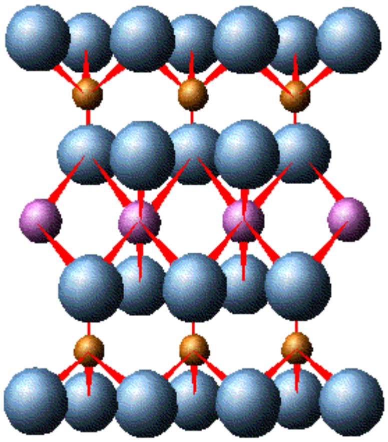

Fig 2.4 One unit cell of pyrophyllite

2.2.2 Effect of heat on clays

As clay is heated a series of physico – chemical changes take place. In case of kaolinite based clays, adsorbed moisture is eliminated round 100°C (Physical water). Organic impurities usually oxidize in the temperature range 300 – 500°C. Next, chemical water is eliminated from kaolinite molecules in the temperature range 500 – 700°C:

$Al_2O_3.2SiO_2.2H_2O = Al_2O_3.2SiO_2$ (meta-kaolinite) + 2 H_2O

This reaction is associated with a theoretical weight loss of about 13.95%. In practice, this loss ranges from 7 to 13% depending on the type of clay mineral involved. At about 900^{o}C, meta-kaolinite decomposes to mullite ($3Al_2O_3.2SiO_2$) and cristobalite (SiO_2) according to the reaction:

3 ($Al_2O_3.2SiO_2$) = $3Al_2O_3.2SiO_2$ + 4 SiO_2

Actually, there is much controversy regarding this reaction since $\gamma - Al_2O_3$ is formed at that temperature which suggests first a decomposition of meta-kaolinite to alumina and silica followed by a solid state reaction between part of the silica formed with alumina to form mullite. In theory, on further heating a liquid will be formed around 1600^{o}C. Final melting will take place at about 1900^{o}C. In practice owing to the presence of fluxing impurities like sodium, potassium, calcium and iron compounds, melting takes place at much lower temperatures.

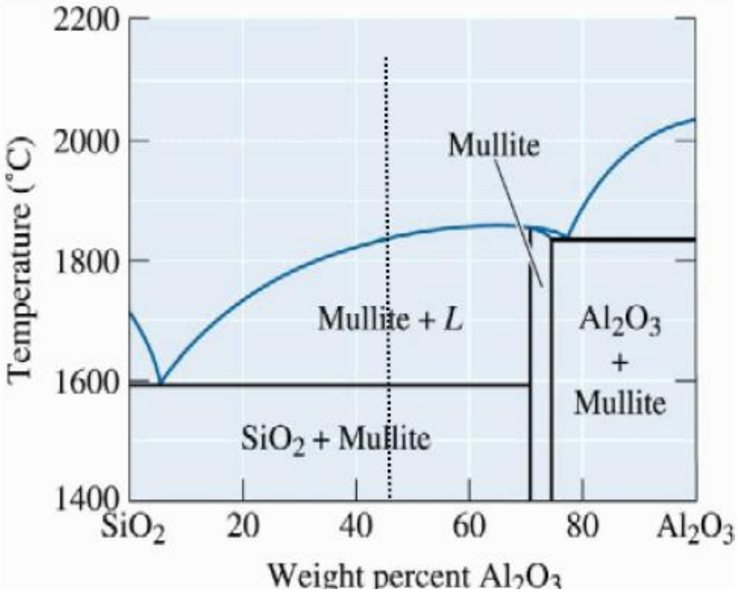

Fig 2.5: The silica – alumina system

2.2.3 Clay ores

In traditional ceramic industries, two main types of clays are used, namely, kaolin clay and ball clay. Occasionally, bentonite clay is added in minute amounts to promote plasticity.

(i) Kaolin clays

This type of clays is of metamorphic origin. It originated from the weathering of igneous rocks over hundreds of millions of years. Consequently, it does not contain much organic impurity and is usually white colored. However, owing to the absence of organic impurities, it suffers from a relatively low plasticity. One factor that adds to that problem is the possible presence of non – plastic sand in levels that may reach 40%. Also, the percent alumina in kaolin clay determines its refractoriness ranging from 25 to 35% according to the level of sand impurities present. Kaolin clays are usually quarried in open pits quarries.

(ii) Ball clays

This is a sedimentary type of kaolinitic clays that has been transported over very long distances, usually by water, to form deposits of often impure clays. The main impurities are of organic origin owing to vegetable and animal debris that have been collected by the material. This imparts high plasticity to the sedimentary mass that makes it often necessary to blend it with other types to promote workability. Also, the long distance travelled by that clay type causes a gradual reduction in the size of its particles due to their crumbling. Increased plasticity as well as reduced particle size confers a high drying shrinkage of the wet products from the forming step. This, in turns, produces dried articles with elevated dry strength although often of deformed shape. Most ball clays are quarried from open pits although being sometimes obtained from tunneled mines. The latter types are generally of higher purity than the former.

(iii) Bentonite clays

This type is a pyrophyllitic type clay that is related to the mineral **montmorillonite** of chemical structure $(Na,Ca)_{0.33}.(Al,Mg)_2.Si_4O_{10}(OH)_2.nH_2O$. Bentonites are usually named after the dominant cations present. Common types are sodium bentonite, potassium bentonite and calcium bentonite. It is added in small amounts (< 1%), to ceramic mixes to promote plasticity. The main uses of bentonite are in drilling mud and as a powerful adsorbent owing to the fineness of its particles. Bentonite clay is known to swell in spectacular way in presence of water. This property is made use by adding it in minute amounts to concrete mixes exposed to running water to decrease their porosity as it swells in contact with water. The same property finds application in foundry sand castings where small amount of bentonite are blended with the sand molds.

(iv) Shale clays

This is a type of low purity sedimentary clay in which the percent of clay minerals can be as low as 60%. The main impurities present are quartz (about 30%), feldspars (about 5%) and iron oxides (about 1%) besides organic matter with variable levels. Its mineralogical constitution is usually of the kaolinite type although some sediment can also contain montmorillonite type minerals. Its use is restricted to low cost articles in which whiteness is not a prime prerequisite like pots and building bricks.

(v) Flint clays

This is a type of sedimentary clay of kaolinitic nature that is usually found in conjunction with coal layers, often in coastal areas. It does not slake in water and is often associated with high levels of silica. This type of clay has a low content of fluxing oxides making it a suitable raw material for refractory brick making. Deposits of high purity constitute a category known as **refractory clays** that possess elevated melting points.

2.2.4 Impurities present in clay ores

Clays are more often than not of low purity, particularly the sedimentary types. These impurities strongly affect their properties in positive or negative ways. The main impurities usually associated with clay ores are discussed in what follows:

(i) Silica

Silica is by far the most common impurity associated with clay ores where it normally exists in the form of quartz. Its presence imparts less plasticity to clay making it less workable besides causing severe abrasion to metallic parts in the shaping equipment. It also reduces the drying shrinkage thus producing dry articles with low mechanical strength. The percent silica in clays depends also on the clay origin. Desert clays tend to contain high levels of quartz sometimes exceeding 40%. The percentage silica present in a clay ore can be evaluated by a test known as determination of free silica.

(ii) Iron impurities

Iron is present in some clay deposits, particularly of the sedimentary type in the form of goethite (FeO.OH) or hematite (Fe_2O_3). The percent iron oxides can constitute up to 7% of the clay composition. Its presence has a fluxing effect on the clay, decreasing the temperature for melt formation. It also imparts a yellowish to reddish color to the fired products shifting even to brown if the level of iron oxides is very high. In fired articles that require a high level of whiteness, Fe (III) reddish compounds are reduced to the almost colorless Fe (II) state by lowering the partial pressure of oxygen in the firing kiln.

(iii) Alkali compounds

Residual clays were formed, as stated before, by the weathering action of igneous rocks. These rocks are constituted of granite, feldspars and mica. Incomplete weathering can result in a clay ore containing sodium or potassium ions due to the presence of feldspathic compounds. The effect of alkalis is to exert a strong fluxing action that reduces the melting point of clay by values that depend on the extent to which they are present.

(iv) Limestone

Limestone, mainly consisting of calcium carbonate, is sometimes present in clay deposits as large veins. Its level does not usually exceed a few percent. Its presence is beneficial in case the clay is to be used in wall tiles making as its presence is essential to prevent remote crazing of tile glazed face. Otherwise, it lowers the plasticity and slightly decreases the melting point owing to its moderate fluxing effect.

(v) Titania

Titania (TiO_2) is essentially present as impurity in sedimentary clays where its content can reach values as high as 4% while it does not usually exceed 1% in residual clays. It confers a greyish color to the raw material and produces a slight fluxing action. Clays containing large amounts of such impurity cannot be used whenever whiteness of the end product is a prime prerequisite.

(vi) Organic matter

The organic matter present in clays, particularly those of the sedimentary type, usually consists of a number of substances such as humic acid and fulvic acid. Both are not a single acid, but rather a complex mixture of several acids produced by the biodegradation of dead organisms. They both contain carboxyl and phenolic groups to different extents. They have been known to increase clay plasticity since several millennia.

2. 3 Non – plastic raw materials

2.3.1 Silica

(i) Allotropic forms of crystalline silica

Silica occurs in three main allotropic forms. The form that is abundant in nature is α-quartz, simply known as quartz. It consists of trigonal crystals that transform to hexagonal (β-quartz) when heated above 573°C. This type of transition is very rapid and reversible. It does not however involve much change in the crystals dimensions: For α-quartz, a = 49.13 nm and c = 54.05 nm while for β-quartz, a = 50.1 nm and c = 54.7 nm. That type of allotropic change is known as a **displacive transition**. When slowly heated in presence of some oxide impurities β-quartz converts to another polymorph: High tridymite. This transformation is sluggish and irreversible. It involves a complete breakdown of the structure and is therefore termed **reconstructive.** High tridymite forms as hexagonal crystals that convert to orthorhombic on cooling down below 160°C (Medium tridymite). On further cooling below 105°C, a third monoclinic polymorph is formed: Low tridymite. These transitions are of the displacive type and hence occur rapidly and reversibly. When slowly heated above 1470°C, tridymite converts irreversibly to a cubic form, known as β-cristobalite. This form can directly be obtained from pure β-quartz when heated above 1490°C. β-cristobalite when cooled below about 200°C transforms reversibly to a low temperature tetragonal form: α-cristobalite. These polymorphic transformations are illustrated in Figure (2.5).

The different forms of silica undergo volume changes upon occurrence of the aforementioned transformations. These are illustrated in Figure (2.6). This figure shows that the displacive transitions are accompanied by relatively large expansion values. Quartz transition is accompanied by about 1.4% increase in length while the corresponding values for tridymite and cristobalite are 0.95% and 1.75% respectively. Such dimensional changes have a direct impact on the operating conditions of firing kilns in the manufacture of ceramic articles.

(ii) The role of silica in the manufacture of ceramic products

Silica plays a dual role in the manufacture of ceramic products and tiles in particular. First, being of non – plastic nature, it decreases the drying shrinkage of unfired articles. Too much silica, however, decreases the dry strength besides causing severe abrasion to metallic parts of the forming equipment. Besides, during firing and in presence of fluxing oxides, silica assists the formation of a highly viscous liquid that slowly diffuses into the pores of the body. On cooling, this liquid transforms into a glassy phase that pulls the particles together causing a firing shrinkage that imparts high strength to the fired body. This bond formed between the particles is called the **ceramic bond**.

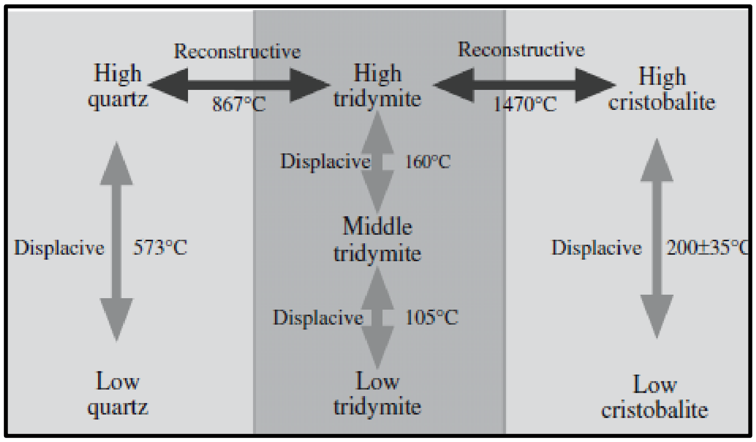

Fig 2.5 Polymorphic forms of silica

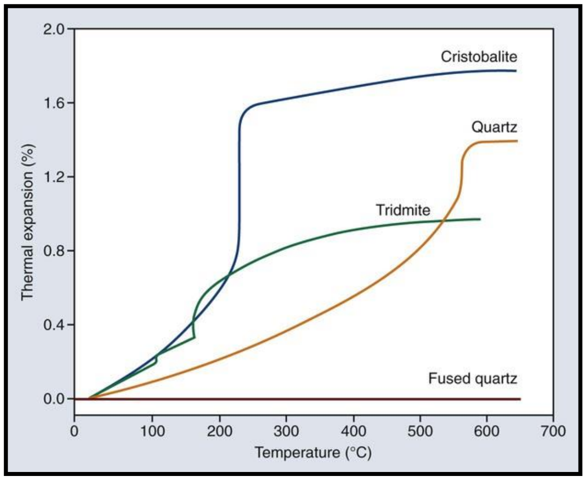

Fig 2.6 Volumetric changes accompanying allotropic transitions of silica

(iii) Silica ores

- **Quartz crystals:** The purest type of silica can be found in the form of well-shaped crystals. This is used in the manufacture of quartz type watches and in piezoelectric applications. Smaller bonded pure grains, called **quartzite**, are used in the manufacture production of refractory bricks. If these bricks are made of pure silica, they are used in the roofs of glass melting furnaces, their commercial name being Dinas bricks.
- **Quartz sand:** This consists of lightly bonded quartz grains, usually of high purity and relatively low particle size. It is essentially used in glass manufacture.
- **Flint:** This is a microcrystalline variety of silica, usually found in the neighborhood of sea shores. It is used in the manufacture of whiteware products.
- **Diatomite:** Also called diatomic earth or kiezelguhr, this variety has evolved over millions of years through the decarbonization of primitive living organisms constituted of two cells. Over the millenia, there occurred a slow replacement of carbon atoms by silicon atoms finally yielding an extremely porous type of silica. That is why it is mainly used as an adsorbing material, as filter aid, in packaging and in a lot of other applications.
- **Common sand:** This is usually contaminated with iron oxides, giving it its yellowish color. It is used in the manufacture of concrete and foundries.
- **Silica fume (flour):** This is an amorphous form of silica obtained as by-product of the ferrro-silicon industry. It is composed of very fine particles of few microns size and usually possesses a narrow particle size distribution. It is mainly used as an addition to concrete since it reacts with calcium hydroxide present in its pores forming hydrates of calcium silicates that impart elevated strength. Its addition to ceramic tiles has proved to be deleterious as it crystallizes to cristobalite followed by rapid grain growth.

2.3.2 Feldspars

Feldspars are alkali or alkaline earth aluminum silicates. They are used as fluxing agents in the ceramic industry. They are non-plastic and their addition decreases the drying shrinkage of the body. They are of moderate grindability, being easier to grind than quartz but more difficult than clays. There are three main types of feldspars:

Albite or soda feldspar: $Na_2O.\ Al_2O_3.6SiO_2$,

Orthoclase or potash feldspar: $K_2O.\ Al_2O_3.6SiO_2$

Anorthite: $CaO.\ Al_2O_3.2SiO_2$

Their fluxing power decreases in the order: K > Na > Ca, that is why; anorthite is seldom used as flux in ceramic industries.

Their presence in a ceramic body allows lowering the firing temperatures and in presence of silica, a viscous melt can be partly formed at a relatively low temperature. This will form the ceramic bond upon cooling the fired body.

More often than not, the quarried feldspars are not purely sodic or potassic; rather they are formed of a solid solution of both. Sometimes, feldspars are present in solid solution with nepheline (K, Na) Al SiO_4, in which case it is considered to be a feldspar – like material (feldspathoid) known as **nepheline syenite.**

2.3.3 Carbonates

The carbonate that is mostly used in ceramic industries is calcium carbonate present in high proportions in limestone, where its percentage can reach 99%. This is a major ingredient used in wall tiles recipes where it is added in levels reaching 20%. Since it decomposes at temperatures in the range 800 – 900^{o}C, the evolution of carbon dioxide may cause troubles in the production line, which requires careful monitoring of operating conditions in firing kilns. Dolomite, a solid solution of calcium and magnesium carbonate is rarely used instead of limestone only if this latter is not readily available.

Calcium carbonate is also the main raw material in cement manufacture while sodium carbonate is used in the production of glass.

2.3.4 Alumina

Aluminum oxide occurs naturally as **corundum**, a very pure oxide ore, **gibbsite**, essentially $Al(OH)_3$, but more commonly as **bauxite**, a hydrated oxide often contaminated with iron oxides. Alumina is extracted from bauxite through a process known as the Bayer process. It is used as a refractory material for making crucibles, bricks, blocks, spark plugs etc…It has not been possible to detect any bauxite on the Egyptian territory.

2.3.5 Zircon and zirconia

The chief source of zirconia (ZrO_2), is zircon ($ZrSiO_4$). It is locally found in black sand, in the Rashid region, in north Egypt. The pure ore is used as an electrical insulator. The oxide, on the other hand, is extremely refractory (M.P. = 2700^{o}C) and is used alone or in association with other oxides (like alumina and silica) to manufacture the refractory lining of glass melting tanks. It suffers, however, from a main drawback, as it undergoes an allotropic inversion at about 1170^{o}C, accompanied with a large volume change. Stabilized zirconia is obtained by adding CaO, in levels from 10 – 20%, which forms a solid solution of reasonable volume stability. Zirconia is also used in the manufacture of piezoelectric ceramics.

2.3.6 Grog

Grog is a synthetic raw material obtained by calcining kaolin above 800°C. This way, the non-plastic meta-kaolinite is formed. This is used as an addition to conventional mixes to reduce shrinkage. Its merit over sand is that, being soft, it does not cause any abrasion of metallic machinery used in the manufacturing processes. On the other hand, it is an essential ingredient in the manufacture of aluminum silicate refractory materials. More often than not grog is obtained by fine crushing of defective unglazed fired products.

Suggested additional reading

1. F.H. Norton, *Elements of Ceramics*, Mc Graw-Hill ed., 1968
2. W.E. Worrall, *Ceramic Raw Materials,* 2nd ed., Pergamon Press, 1982
3. B.V.S. Subba Rao, *High Performance Ceramics,* Proceedings of the seminar on high performance ceramics, Hyderabad, 1987
4. C.B. Carter and M.G. Norton, *Ceramic Materials,* 1st ed., Springer science, 2007