

CHAPTER II

LITERATURE REVIEW

2.1 Terra-cotta

The name “terra-cotta” (19) comes from Italian word, means clay firing. It is an earthenware fired at low temperature about 900-1000°C. The majority of terra-cotta includes 10-15% porosity. This material has a large size and is made from clay and grog. The clay body is prepared from local clay or red clay, which is easy to form and contains high percentage of ferric oxide. Terra-cotta has a number of attractive features, such as a large variety of surface colors and textures. After firing, color of clay body becomes orange or red-brown such as terra-cotta pottery shown in Fig. 2.1.

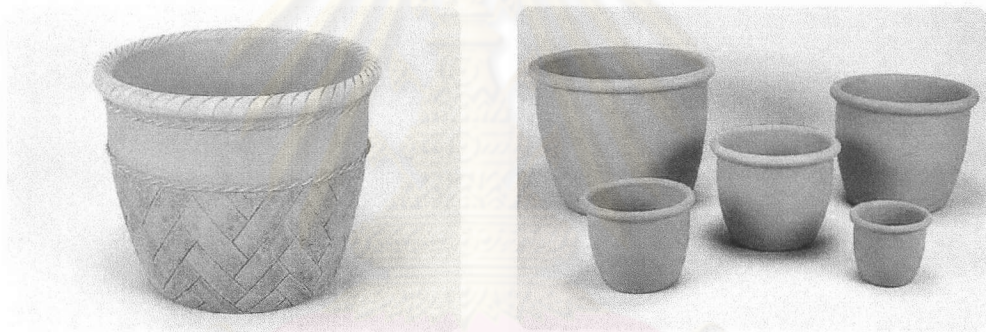


Fig. 2.1. Terra-cotta pottery.

2.2 Fluxes

Flux is a substance that is added to a body to decrease melting temperature. In ceramics, particularly in pottery industry, fluxes are incorporated in the body in order to lower the firing temperature by promoting liquid phase formation that facilitates the densification during firing. The liquid phase surrounds the solid particles and by surface tension attracts the particles and closes the porosity. This liquid forms a glass when it is cooled and binds the grains of the body together. As a result the strength of the fired body increases and water absorption decreases. It is not desirable to lower the softening point further, since the higher proportion of liquid formed would cause the deformation of shape after firing.

For siliceous materials the most effective fluxes are alkali oxides such as Na_2O , K_2O and Li_2O . Calcium and magnesium oxides also act as fluxes, normally in combined form. (20-21) They may be present as impurity in raw materials or more frequently may be deliberately added to the body. The most widely use fluxes are feldspars, wollastonite (CaSiO_3), nepheline [$\text{Na}(\text{AlSi})\text{O}_4$], and bone ash (used in bone china bodies). Some kind of clay contains enough natural flux to allow them to be used for their purpose without addition of extra fluxes, e.g. stoneware clays contain natural fluxes such as mica, feldspar, lime, and magnesia, and can be fired at $1200\text{-}1300^\circ\text{C}$ to give a vitreous body without addition of further flux. Similarly building bricks are made from clay containing enough natural fluxes to give strength to the brick when fired at about 1100°C . However cost and availability are the main factors that influence the choice of materials.

2.3 Forming of stiff plastic body

Stiff clay bodies are usually formed by extruding through a die, continuously by an auger or intermittently by a plunger. Long pieces of simple or complicated cross section may be made in this way and later cut into short sections for brick, block, or pipe.

2.3.1 Auger extrusion

Fig. 2.2 (19) shows a cross section of a vacuum auger with the parts labeled. The mixture is fed into the top where it is kneaded by the blades of the central shaft and at the same time forced through a series of small openings into the vacuum chamber. It is picked up by another auger shaft and forced through the die, which is often heated and lubricated to reduce friction. The column from the die is carried on a moving belt or carriage and cut into the desired length, often by one or more stretched wires.

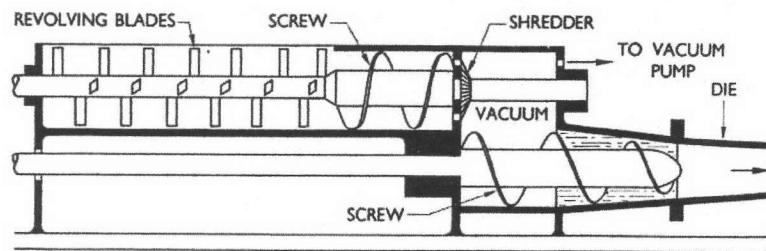


Fig. 2.2. Cross section of a vacuum auger. (19)

Inserts are placed inside the die to produce hollow columns such as drain tile or perforated brick. The auger can be a high production machine turning out as much as 10 tons per hour.

2.3.2 Piston extrusion

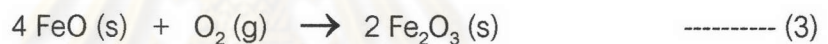
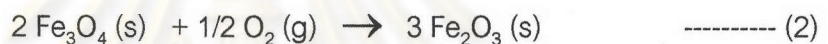
In this operation a cylinder is filled with shredded, stiff plastic body, which is forced out through a die to form a column of uniform cross section that may then be cut into the desired lengths. Sometimes the cylinder is evacuated after filling. This process gives a more uniform column than the auger, but there is still a density difference between the exterior and center of the column.

Piston extrusion is used for fine-grained refractories and electronic bodies. The body may be placed in the cylinder as a preformed slug and forced through the die at pressures up to 5000 psi. Another method adds the shredded body with a wax binder to the cylinder, evacuates the cylinder, and forces the body through the die.

Large sewer pipes are made in a vertical piston extruder. The evacuated cylinder is filled with clay from an auger, a steam-driven piston forces the clay through an annular die into a fixture to form the bell, after which a length of pipe is extruded and cut off with a wire.

2.4 Fired color

Iron oxide is the most important and variable colorant in all structure clay products. It is present in most clay from 1% to 8%. In some cases extra iron oxide may be added to intensify its coloring effect. The hematite (Fe_2O_3) is red in color and is responsible for the various shades of the red colors. (22) When it is reduced by carbon monoxide, the form of iron oxide can be either magnetite (Fe_3O_4) or ferrous oxide (FeO) both of which are black in color at all temperatures, as show in reaction (1). Reduction of the red ferric oxide to the black ferrous oxide will result if carbon monoxide is present in the kiln atmosphere. Carbon monoxide results when there is insufficient oxygen for the complete combustion of the fuel.



Excess oxygen maintains iron oxide in the ferric oxide state according to the reaction (2) and (3). This is the red shade of iron oxide but color varies from orange to purple, depending on the temperature to which it is fired (lighter colors are produced at the lower temperatures). Fig. 2.3 (23) shows the stability domains of the various phases in Fe-O system.

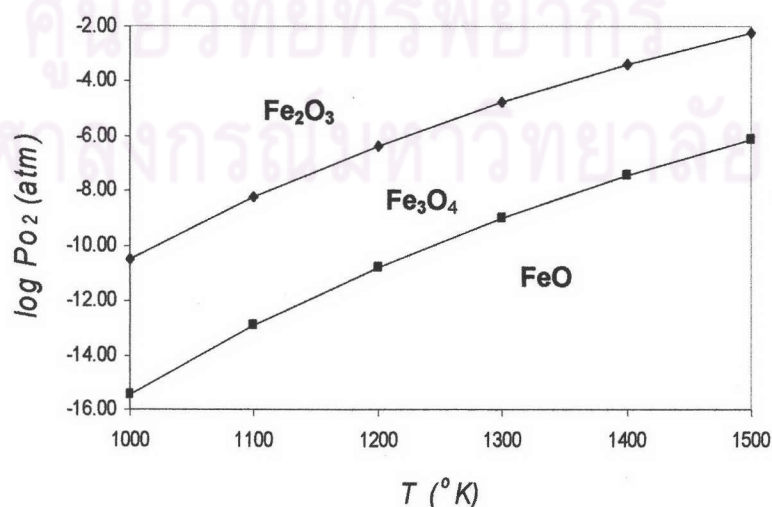


Fig. 2.3. The stability domains of the various phases in Fe-O system. (23)

In the highest oxidation state, hematite is produced, and its color is temperature dependent. The color of hematite derives from a defect crystal structure, and the number of defects per unit of volume increases with temperature. (24) The development of defects is a reversible reaction, but the rate of removing defects is very slow in air than the production of defects on heating. At low temperature, Fe_2O_3 is orange in color and, as the temperature increases, it changes to darker reds and finally the color becomes black at 2400°F (1316°C). Reduction of iron oxide at high temperature is often used to produce tan, brown, and black products from red-firing materials.

Fired clay products can be made in pink and light red colors. It can be explained on the basis of the ability of Fe^{3+} ions to enter the mullite crystals by substitutional solid solution. (24) Fe^{3+} plays the role of Al^{3+} in mullite to a limited extent. When iron enters mullite, the white color of mullite is changed to light yellow. At 1100°C mullite can take 1.2% by weight of Fe_2O_3 into a solid solution, 3.8% at 1200°C , and 7.6% at 1300°C . This solid solution reaction between mullite and Fe_2O_3 removes the red hematite phase from the body when sufficient amount of mullite has been developed to accommodate all the iron oxide present, thereby eliminating its characteristic red color. (25-28)

2.5 Water-ice behavior

Seventy-one percent of the earth's surface is covered with water. It appears that most of the material of the universe is either solid or gaseous. A water molecule is formed when two atoms of hydrogen bond covalently with an atom of oxygen. In a covalent bond electrons are shared between atoms. In water the sharing is not equal. The oxygen atom attracts the electrons more strongly than the hydrogen. This gives water an asymmetrical distribution of charge. Molecules that have ends with partial negative and positive charges are known as polar molecules. It is this polar property that allows water to separate polar solute molecules and explains why water can dissolve so many substances.

The normal pattern for most compounds is that as the temperature of the liquid increases, the density decreases as the molecules spread out from each other. As the temperature decreases, the density increases as the molecules become more closely packed. This pattern does not hold true for ice as the exact opposite occurs. In liquid water each molecule is hydrogen bonded to approximately 4.4 other water molecules. In ice each molecule is hydrogen bonded to 4 other molecules. As water freezes, its molecules form a latticework of hexagons that contain empty space. The empty spaces within the ice structure, as this translates to a more open or expanded structure. (29) These hexagons cause water to expand 9% in volume according to density as shows in Fig. 2.4. This increase causes enough force to break most rigid containers. This is the same force, repeated on a daily basis, which creates "pot holes" in the roads in the winter time.

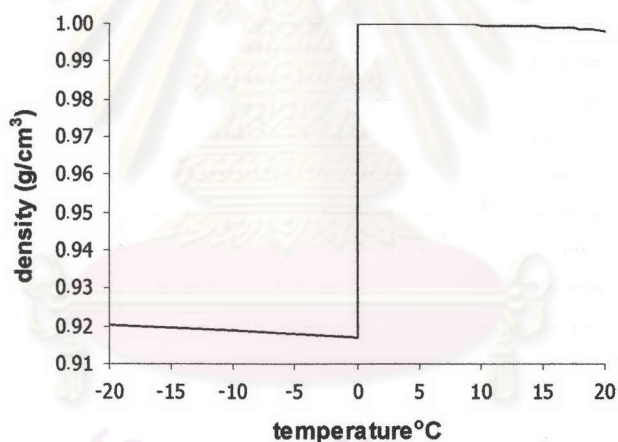


Fig. 2.4. Water-ice density (g/cm^3).

Ice is the solid form of water. The phase transition occurs when liquid water is cooled down to 0°C (273K , 32°F) at standard atmospheric pressure. Ice, water and water vapor can coexist at the triple point, which for this system is 273.16K at a pressure of 611.73 Pa as show in phase diagram of water in Fig. 2.5. (30) When 'x' point is a typical room temperature and pressure.

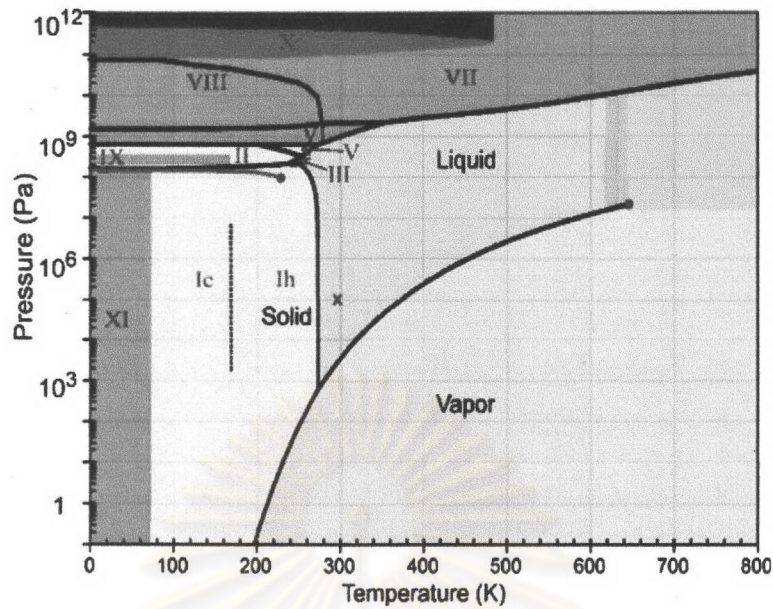


Fig. 2.5. The phase diagram of water. (30)

The most basic form of ice and snow crystal is a hexagonal prism or hexagonal ice (density is 0.92 g/cm^3), called ice Ih according to Fig. 2.6. (31) Note that the hexagonal prism can be "plate-like" or "column-like", depending on which facet surfaces grow most quickly. Ice can form in roughly a dozen different phases. (30) Only a little less stable (metastable) than ice Ih is cubic structure ice (ice Ic, density is 0.92 g/cm^3). The types of ice are differentiated by their crystalline structure, ordering and density such as ice XI, density is 0.92 g/cm^3 and orthorhombic crystal.

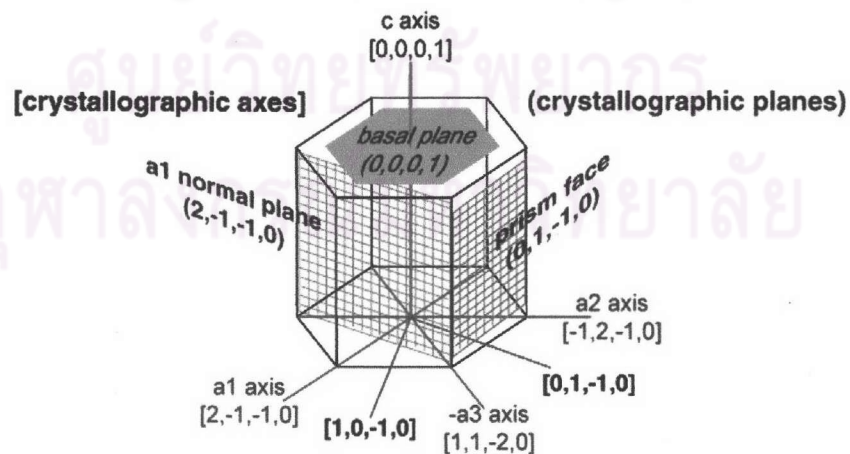


Fig. 2.6. Ice hexagonal crystal. (31)

2.6 Frost heaving

Frost damage is the result of tensile stresses caused by the freezing of water in the pores of the matrix. The saturation state and water distribution are functions of the porous media geometry. (32) Under natural conditions, the water content is the result of a capillary imbibitions or a sorption from total immersion. (33) This saturation state influences the degree of frost damage.

Water in the porous systems, based on its interactions with the pore walls, could be present in three different states as free water, bound water (adsorbed water) and capillary water. Free water is present in macro pores are usually leaks out due to the force of gravity or evaporates, leaving a free space for ice expansion ($\Delta V = 9\%$). It has connection with bound water in micro pores and capillary pores live in the micro pores. The water transport properties are controlled by the permeability of the material. The water sorption of porous material under natural conditions is caused by either capillary imbibition or sorption from total immersion as Poiseuille's law according to equation (1).

$$\frac{dX}{dt} = \frac{\sigma \cos \Theta \cdot r}{4\mu X} \quad \text{----- (1)}$$

Where X is the distance from the free surface; σ is the surface tension of the water-air interface; Θ is wetting angle; r is radius of the capillary; μ is the fluid viscosity. This simple model shows an increase of flow as a function of the capillary size. (34) Water freezing temperature point changes in capillary pores due to capillary forces, or due to the influence of physical adsorption forces. These forces increase with the decrease of pores radius (35) as illustrated in Fig. 2.7. (36)

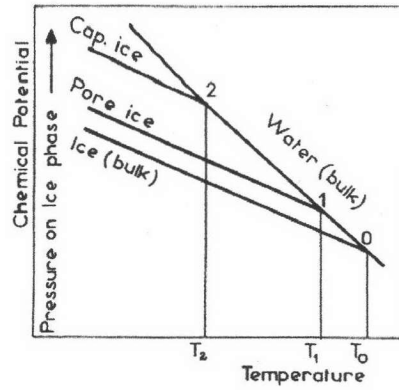


Fig. 2.7. Chemical potential diagram of freezing of water. (36)

At constant temperature the chemical potential of the ice increases with its state of dispersion; the change is associated with the increase in pressure in the ice phase according to equation (2). (37)

$$\mu_{cap\ ice} - \mu_{bulk\ ice} = \bar{v}_i (P_{cap\ ice} - P_{bulk\ ice}) \quad \text{----- (2)}$$

Where \bar{v}_i is the partial molar volume of ice; μ_{ice} is the chemical potential of ice. Fig 2.6 shows a model consisting of a porous cavity connected to a water source by a fine capillary. Equation (2) results in a shift of the chemical potential of the ice with increasing dispersion: $\mu_{cap\ ice} > \mu_{pore\ ice} > \mu_{bulk\ ice}$. Thus, capillary ice cannot form at 0°C , and a supercooling $T_2 - T_0$ is required for the formation of ice in the capillary. On the other hand the water in the larger pores can freeze before the water held in smaller pores. Therefore, refreezing of entrapped water in capillary pores, resulting from the ice phase in micro pores, develops a tensile stress as equation (3) that cause of frost damage. (38)

$$p = \frac{Q_f \cdot \Delta T}{T(V_w - V_i)} \quad \text{----- (3)}$$

Where P is a tensile stress; Q_f is latent heat of fusion of ice; V_w, V_i is specific volume of water and ice; ΔT is supercooling.

During the freeze-thaw procedure, ceramic material is exposed to a loading cycle created by the tensile stresses developed by the action of ice. In the case of calcareous matrix, damage can appear at the junction between micro pores and

capillaries, if the pressure rises beyond the local pore wall strength. The pressure increase is higher for thinner capillaries. Consequently, the damage is potentially greater during the passing of an ice front through such small capillaries. The water flow, pushed back by the freezing front into the capillary, can induce hydraulic pressures and the development of secondary stresses. (39) Therefore, the coarse pores (in the micrometer range) are considered favorable to frost resistance and finer pores dangerous. (40)

In most cases, the material is partially saturated under natural conditions. Air is trapped in the large pores that are not connected to the outside. If the water-air interface is located at the throat of such pores, excess pressure in the capillary network is dissipated by compressing air into the pore. The presence of trapped air in large pores protects the material from frost damage, due to the decrease of pressure in the ice and to the scattering of stresses by air compression. (41) Frost resistance is thought to be determined by a combination of variables, no single parameter seems to determine it completely.

2.7 Literature survey of frost resistance property

Most of the work on frost damage of porous materials has been done on concrete, brick and soils.

In 1972, G.G. Litvan (42) determined the dimensional changes and the thermograms of cement specimens during temperature cycles ($+5^{\circ}\text{C}$ to -60°C , $0.33^{\circ}\text{C}/\text{min}$). Freezing processes at -8°C and -40°C and melting processes at -11°C and 0°C were observed. At higher temperature, freezing occurs on the outer surface and at the lower temperature, it occurs in the pores after redistribution of the water.

In 1974, Blanchere and Young (36) pointed out that the freezing of water in a clay body has been observed to occur in two stages, and introduced the role of capillary-shaped pores. First, water freezes in large pores at about 0°C . Second, water freezes in the capillaries when the temperature is between about -2°C and -8°C . Generally, more expansion takes place during capillary water freezing than by the

freezing of water in large pores. They concluded that higher resistance brick has a lower pore volume, a narrower pore size distribution and large average pore diameter.

In 1976, Brownell (23) indicated that frost resistant brick have an average pore diameter of 1.6 μm , whereas the low frost resistant brick have an average pore diameter of 0.24 μm .

In 1988, N. Masahiko (43) determined frost deterioration of brick specimens by cyclic freezing and thawing under unidirectional flow. Because ceramic building materials are usually used under heat transmitted unidirectional conditions. Rectangular samples (2.0 by 2.5 by 1.8 cm) were cut from a brick. Samples were saturated with a 5% NaCl brine, was used to accelerate frost action, by immersion for 24 h at room temperature. The testing apparatus was performed automatically using a personal computer. The test results show laminar cracks appeared perpendicularly to the cooling surface, but in the freezer test radial cracks developed due to internal expansion by water entrapped in a center part of the sample.

In 2001, Mikulas Sveda (44) summarized the methods of frost resistance test in brick. These methods can be divided essentially into two groups: direct methods and indirect methods. The direct methods is based on the direct freezing of samples, after which the change of some parameters. The disadvantage of the direct methods is expensive and long duration of the test. Therefore, there is the tendency to use indirect methods which can be divided into three groups. The first group evaluates the frost resistance according to the criteria of water absorption and the percentage of pore volume at a particular pore diameter. The second group is according to the pore cumulative lines or the line of pore size distribution. The third group is according to mathematical formulas. The most important parameters are usually pore volume and percentage of pore volume at particular pore diameters. His results are as follows, (1) Frost resistance is substantially affected by the mineral composition of the brick clay. (2) Modification of pore volume alone does not influence frost resistance. (3) Frost

resistance is greatly affected by the pore radius median that increases with an increase of the pore radius median at constant volume.



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