CHAPTER 2
LITERATURE REVIEW

Archaeological kiln site was the place for production of ceramics in the past. It was thus interesting to study about ceramic process in human history. In upper Northern Thailand, the Lan Na region, Lan Na is called for the ancient Thai kingdom of AD. 1292 – 1558 period [7]. The kingdom was founded by King Phaya Mang Rai and capitalized in Chiang Mai. Territory of the kingdom covered the area of present northern region of Thailand including Chiang Mai, Lamphum, Chiang Rai, Phayao, Phrae, Nan and Mae Hong Son provinces. Ceramic kiln site is recognized as one of the most important archaeological and historical resources of Thailand. An excavation of kiln sites recently discovered at Sisatchanalai or Sawankhalok, Sukhothai province of 12th – 16th century AD [8]. In upper north of Thailand there are at least 13 known ancient ceramic kiln sites, there are:

1. Wiang Kalong kiln site, Chiang Rai province.
2. Wang Nua kiln site, Lampang province.
3. Sankamphaeng kiln site, Chiang Mai province.
4. Phan or Pong Daeng kiln site, Chiang Rai province.
5. Thung Tao Hai kiln site, Lampang province.
6. Wang Hai kiln site, Lampang province.
7. Wang Tha Kaan kiln site, Chiang Mai province.
8. Ban Mae Tao Hai kiln site, Chiang Mai province.
9. Huai Mae Tam kiln site, Phayao province.
10. Wiang Bua kiln site, Phayao province.
11. Huai Nam Yauk kiln site, Mae Hong Son province.
12. Intakhin kiln site, Chiang Mai province.
13. Ban Bo Suak kiln site, Nan province.

The study found that Ban Bo Suak wares were quite similar to Sukhothai and Lan Na wares, especially glaze, decoration technique and shape of wares (Jar mouth-rims and double mouth rims). The characteristics of the Jar were very similar to Lan Na and Sukhothai wares. Lamp of Ban Bo Suak was similar to the Sukhothai one presumed to be produced during the 15^{th}-16^{th} century A.D. During this period Sukhothai and Lan Na started producing underglazed black wares due to the inspiration from the Chinese blue and white wares [8]. The difficulty in studying history of Lan Na ceramics was lack of any absolute dating data which no one could cite as evidence, so the chronology of them was still unconfirmed and confused. Although Lan Na region was abandoned with ceramic kiln sites, history of them were absent from historical evidences such as stone inscriptions, legends, chronicles or oral history. The only method to describe and to write their history depended on archaeological work and scientific research related to them.

2.1 Ancient Nan Pottery

Ban Bo Suak was the community located at Suak sub-district, Muang district, and Nan province in Thailand. Sayan Praicharnjit from Faculty of Archaeology discovered that the first archaeological excavation at the kiln was operated in October 1999 [8]. The kiln was located about 8 km. south-west of present Nan town in the administrative area of Bo Suak sub-district, Muang Nan district of Nan Province (Figure 2.1). Ban Bo Suak was called “Ban Tao Hai Jae Liang”. Archaeological process was firstly developed during the excavation. Two kilns named Tao-Sunan and Tao-Ja-Manas had been unearthed and later displayed in-situ as open-pit museum for visitors. In 2006, the kiln-wasted area of Sunan and Ja-Manas kiln, Saen-Si kiln, Chuen kiln were discovered in the residential area of Ja-Manas. Twin kilns of Manop Tikham, 100 m south east of the Ja-Manas kiln were excavated. In 2007, Sayan Praicharnjit excavated the kiln site at Doi Fuang Moh in the area where large numbers of stoneware saggar were found. The excavation indicated that saggar technology was used at the kiln complex during the period of 16^{th} -17^{th} century AD. Kiln remains and ceramic wastes presented in the approximate area of 3-4 km^2 on levee banks of Nam Suak, both sides of a ravine Huay Puan and in the high plain called Doi Fuang Moh and on high plain in the vicinity of Ban Nong Tome. Archaeological evidence at Ja-Manas kiln, Sunan kiln, Saen-Si kiln, Chuen kiln and Manop kiln, indicate that the early phase of ceramic production without saggar technology at kiln complex was during the 13th-15th century AD and the second phase with saggar technology was during the 16th-17th century AD. The calibrated age of charcoal sample from Ja-Manas kiln illustrated in diagram below indicated that the period of AD 1280-1315 (BE 1823-1858) based on the 1 sigma calibrated result with 68 percent probability. This was the acceptable period for the operation of Ja-Manas [8]. Archaeological stratigraphy at Ja-Manas kiln mound indicated that there had been a kiln constructed and operated prior to the construction time of Ja-Manas kiln which meant that the operation of the kiln site would commence at least in the first half of the 13th century AD. The kilns found in all excavated sites were single chambered Lan Na kiln applying overall clay construction built and buried man-made mound [9, 10].

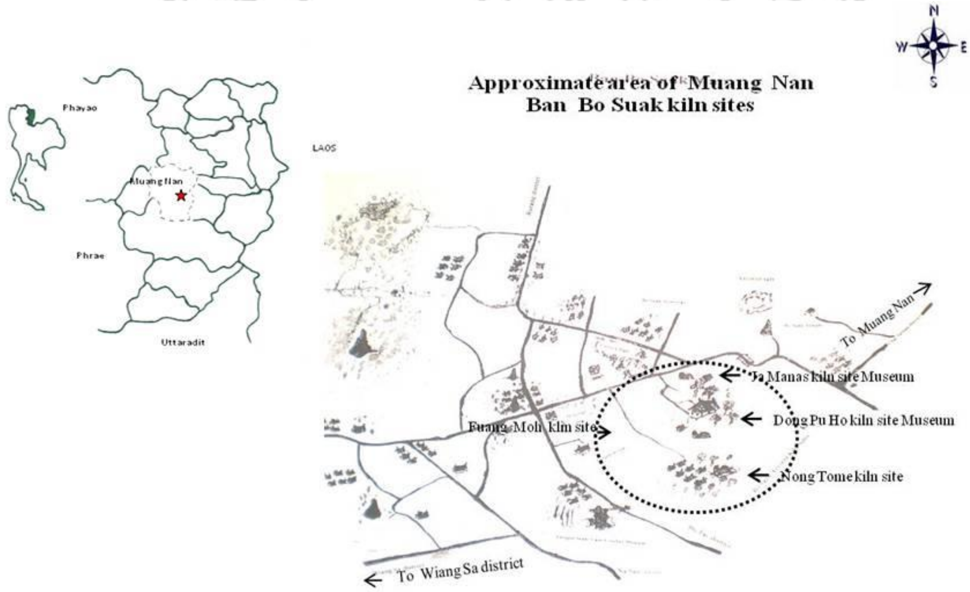


Figure 2.1 Map illustrating locations approximate are of Ban Bo Suak kiln sites.

It was measured 6.50 m long, 3.00 wide and the chamber was 0.8 m. The kiln was a cross-draft kiln (Figure 2.2). Most of the pots were loaded through the front of the firebox. Sunan and Ja-Manas kilns had similar form and size. They were constructed and operated during the period of AD 1280-1350. The fine arts department carried out a preliminary survey and studied of this kiln site. Ceramic products of the kiln were classified in two phases: the first phase during 13th -15th century AD without saggar, and the second phase during 16th-17th century AD with saggar technology [11]. Ceramic production of the first phase produced unglazed stoneware and early green glazed stoneware. Jars were major group of unglazed product of these kilns. Two main categories of jar manufactured here were jars with single mouth-rim and jars with double mouth-rim (Figure 2.3, 2.4). Glaze was intentionally applied over thin layer of engobe on interior leaving exterior unglazed or covering with natural ash glazes. Ceramic production of the second phase unglazed stoneware and early green glazed stoneware vessels including jars and bowls without kiln furniture and ware-supports. New identical technology for kiln setting saggar was practiced only at Bo Suak kiln during the period of the 16th-17th century AD [7, 8]. Its function was used to support and separate the vessel loading/stacking in association with saggar in the chamber of the kiln [12].

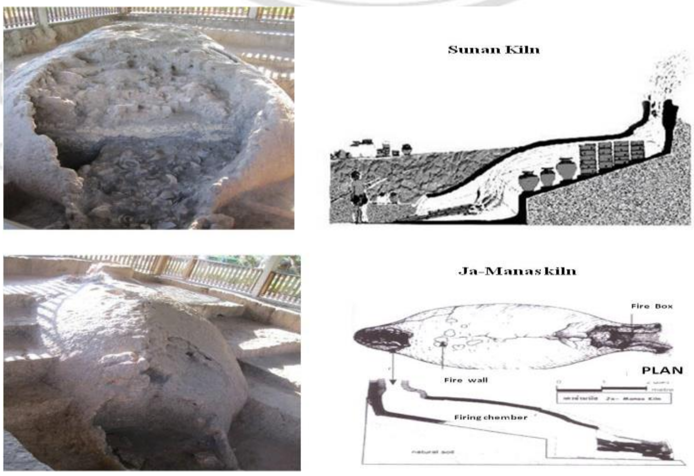


Figure 2.2 Tao Sunan and Ja-Manas kilns after excavation [8].

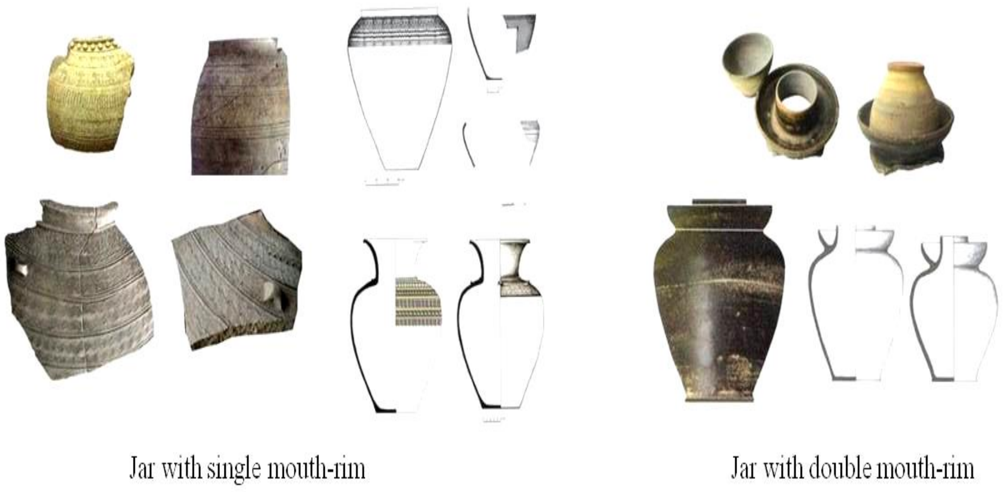


Figure 2.3 Jars with single and double mouth-rim**,** incised decoration body [8].

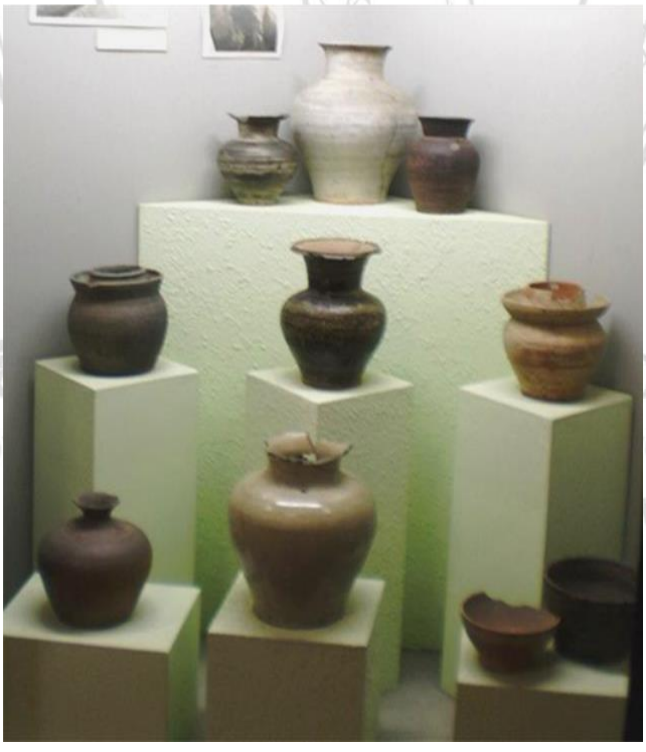


Figure 2.4 Ban Bo Suak potteries from the National Museum of Nan.

2.2 Archaeological theory and method

Dating is process of estimating the age of ancient materials and deposits remains or determining a chronology or calendar of events in the history of Earth. Dating material drawn from the archaeological record can be made by a direct study of an artifact, or may be deduced by association with materials found in the context the item is drawn from or inferred by its point of discovery in the sequence relative to datable contexts. Dating is carried out mainly post excavation, but to support good practice, some preliminary dating work called "spot dating" is usually run in tandem with excavation. Dating is very important in archaeology for constructing models of the past, as it relies on the integrity of datable objects and samples. Many disciplines of archaeological science are concerned with dating evidence.

1. Relative Chronology

Relative methods tend to use associations built from the archaeological body of knowledge. An example is seriation, which may use the known style of artefacts such as stone tools or pottery. Ultimately, relative dating relies on tying into absolute dating with reference to the present.

1.1 Dating by comparing the objects with associated objects or sites.

1.2 Dating by correlating designs or decorations with those on items of known age.

2. Absolute Chronology

Absolute dating methods rely on using some physical property of an object or sample to calculate its age. Examples are:

2.1 By reference written on the surface such as inscription of historic annals or chronicles.

2.2 By means of inscribed or painted dates such as those found on coins and some Chinese pottery.

2.3 The use of scientific methods

2.3.1 Radiocarbon dating: Carbon dating is a variety of radioactive dating which is applicable only to matter which was once alive and presumed to be in equilibrium with the atmosphere, taking in carbon dioxide from the air for photosynthesis. Cosmic ray protons blast nuclei in the upper atmosphere, producing neutrons which in turn bombard nitrogen, the major constituent of the atmosphere. This neutron bombardment produces the radioactive isotope carbon-14. The radioactive carbon-14 combines with oxygen to form carbon dioxide and is incorporated into the cycle of living things. The carbon-14 forms at a rate which appears to be constant, so that by measuring the radioactive emissions from once-living matter and comparing its activity with the equilibrium level of living things, a measurement of the time elapsed can be made. Carbon-14 decays with a halflife of about 5730 years by the emission of an electron of energy 0.016 MeV. This changes the atomic number of the nucleus to 7, producing a nucleus of nitrogen-14. At equilibrium with the atmosphere, a gram of carbon shows an activity of about 15 decays per minute. The low activity of the carbon-14 limits age determinations to the order of 50,000 years by counting techniques. That can be extended to perhaps 100,000 years by accelerator techniques for counting the carbon-14 concentration. Figure 2.5 shows the measurement of decay activity of a buried piece of wood which provides a measurement of the time elapsed since it was alive and in equilibrium with atmosphere [13].

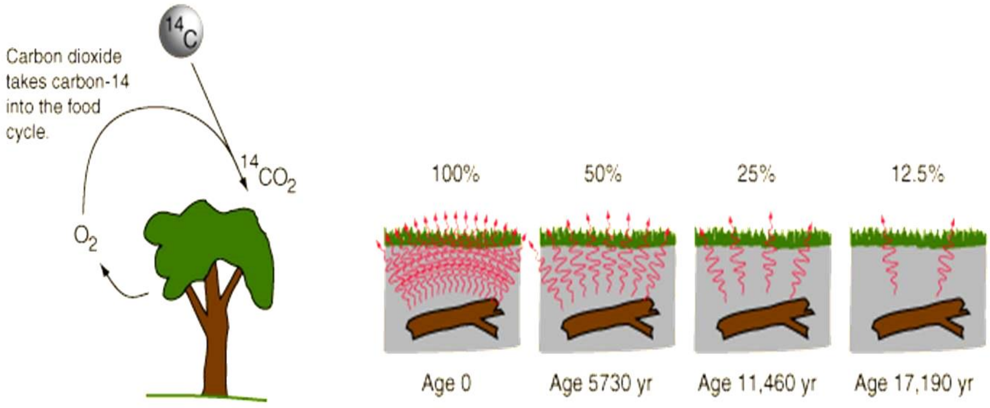


Figure 2.5 Measurement of decay activity of a buried piece of wood.

2.3.2 Thermoluminescene (TL) dating is the determination, by means of measuring the accumulated radiation dose, of the time elapsed since material containing crystalline minerals was either heated (lava, ceramics) or exposed to sunlight (sediments). Crystalline material is heated during measurements when the process of Thermoluminescence starts. Thermoluminescence emits a weak light signal that is proportional to the radiation dose absorbed by the material. The technique has an age range of 1,000 to 500,000 years. Part of the radioactive decay from K, U, Th, and Rb in the soil, as well as contributions from cosmic rays, are trapped over time in sediments. The longer the burial, the more absorbed dose is stored in sediment; the dose is proportional to a glow curve of light obtained in response when the sample is heated or exposed to light from LEDs. Greater light doses indicate an older age.

The sample was irradiated with B source to artificially age of the sample; the sample was preheated and finally heated to 5000 °C in a vacuum oven with a nitrogen atmosphere under a photomultiplier tube. Thermoluminescence techniques (a) a ground up sample were placed in a special oven (b) heat was raised rapidly resulting in an energy emission from the sample shows in Figure 2.6 [14]. The tube measured light emitted by the sample providing an equivalent dose calculation (2.1)

$$\text{Age} = \text{Equivalent Dose}/\text{Dose Rate} \tag{2.1}$$

Thermoluminescence was used in conjunction with U-series, 14C, stratigraphy and associated biological processes whenever possible.

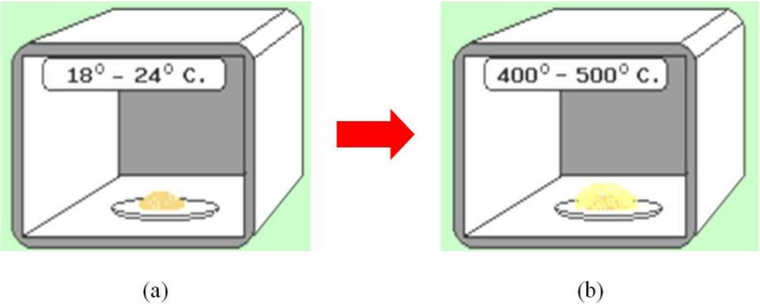


Figure 2.6 Thermoluminescence techniques (a) a ground up sample was placed in a special oven (b) heat was raised rapidly resulting in an energy emission from the sample [14].

3. Stratigraphic relationships

Archaeologists investigating a site may wish to date the activity rather than artifacts on site by dating the individual contexts which represents events. Some of dating objects by their position in the sequence can be made with known datable elements of the archaeological record or other assumed datable contexts deduced by a regressive form of relative dating which in turn can fix events represented by contexts to some range in time. However the date of contexts often falls in a range of possibilities so using them to date others is not a straightforward process. For example, the date of formation of a context which is totally sealed between two datable layers will fall between the dates of the two layers sealing it. Figure 2.7 shows the date of formation of a context which was totally sealed between two datable layers, (a) here we can see 12 contexts, each numbered with a unique context number and (b) sequence is represented in the Harris matrix [15].

1. A horizontal layer
2. Masonry wall remnant
3. Backfill of the wall construction trench
4. A horizontal layer, probably the same as 1
5. Construction cut for wall 2
6. A clay floor abutting wall 2

7. Fill of shallow cut 8

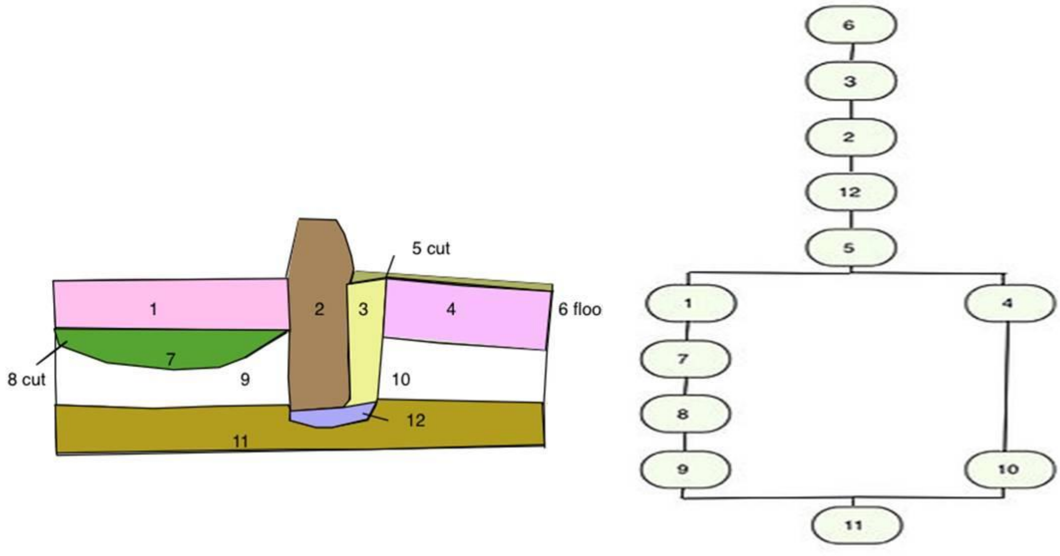
8. Shallow pit cut

9. A horizontal layer

10. A horizontal layer, probably the same as 9

11. Natural sterile ground formed before human occupation of the site

12. Trample in the base of cut 5 formed by workmen's boots constructing the structure wall 2 and floor 6 is associated with.



(a) (b)

Figure 2.7 The date of formation of a context which was totally sealed between two datable layers, (a) here we can see 12 contexts, each numbered with a unique context number and (b) sequence was represented in the Harris matrix [15].

If we know the date of context 1 and context 9 we can deduce that context 7, the backfilling of pit 8, occurred sometime after the date for 9 but before the date for 1, and if we recover an assemblage of artifacts from context 7 that occur nowhere else in the sequence, we have isolated them with a reasonable degree of certainty to a discrete range of time. In this instance we can now use the date we have for finds in context 7 to date other sites and sequences. In practice a huge amount of cross referencing with other recorded sequences is required to produce dating series from stratigraphic relationships such as the work in seriation.

2.3 Ceramic processing

Most ceramic products were clay-based and made from single clay or clay mixed with mineral modifiers such as quartz and feldspar. General classification of ceramics was divided into two groups. Ceramics were defined as a class of inorganic, nonmetallic solids that were subjected to high temperature in manufacture or use. Ceramic products that were made from highly refined natural or synthetic compositions and designed to have special properties were referred to as advanced ceramics. Advanced ceramics could be classified according to application as electrical, magnetic, optical, chemical, thermal, mechanical, biological and nuclear. Traditional ceramics refered to ceramic products that were produced from unrefined clay and combinations of refined clay and powdered or granulated nonplastic minerals. Often, traditional ceramics were used to refer to ceramics in which the clay content exceeded 20 percent. General classifications of traditional ceramics were described below. Pottery was sometimes used as a generic term for ceramics that contained clay and were not used for structural, technical, or refractory purposes. Pottery ware was defined as glazed or unglazed nonvitreous clay-based ceramic ware. Traditional ceramic could be fabricated in various methods. The main process included forming, drying, decorating, glazing, biscuit and firing process. Forming techniques for the traditional ceramic could be divided into two main basic categories. One was hand-building and the other was wheel-building technique. The first step of ceramic forming method was the preparation of the optimal clays. The clay was then formed by using hand-building or wheel-building techniques [16]. Methods of forming: Hand-shaping was the earliest method used to form vessels. This included the combination of pinching coiling and wheel-building [17]. After forming process, green sample needed to be slowly dried to increase strength. Sample was then decorated the distortion of shape. This was the final step for decoration of shape and carved pattern on surface because the sample had high strength after biscuit firing process. Various techniques were applied in decoration, such as scraping, trimming, shaving and turning. Besides, decorative process involved application of the under-glaze to create the imaginative color on surface of dried sample before biscuit firing process [18]. Figure 2.8 shows decorative techniques of Nan pottery (a) unglazed (b) slip decoration and (d) glaze decoration.

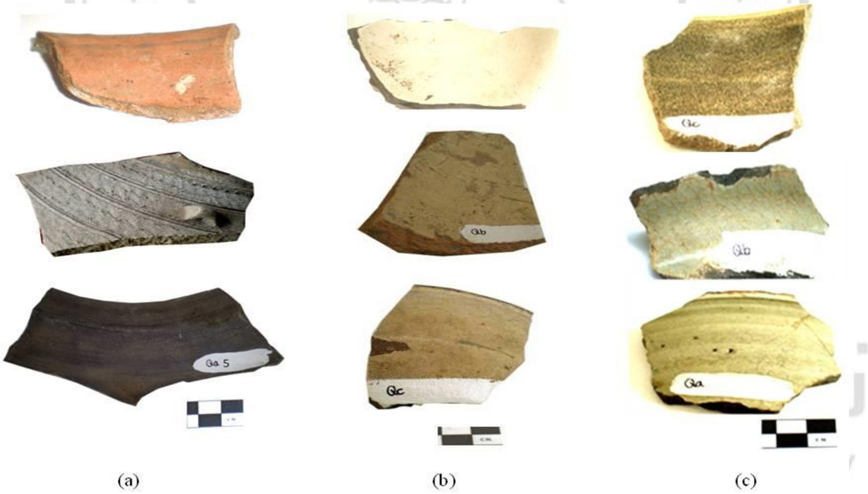


Figure 2.8 Decorative techniques of Nan pottery (a) unglazed, (b) slip decoration and (d) glaze decoration.

Clay is given durability only by firing with high temperature. This is the final stage of the ceramic process. Firing pottery can be done using a variety of methods, with a kiln being the usual firing method. Both the maximum temperature and the duration of firing influence the final characteristics of the ceramic. Thus, the maximum temperature within a kiln is often held constant for a period of time to soak the wares to produce the maturity required in the body of the wares. Clay can be subdivided into five various temperature range groups: earthenware are normally fired at temperatures in the range of about 1,000°C to 1,200 °C, stoneware at between about 1,100 °C to 1,300 °C and porcelains at between about 1,200 °C to 1,400 °C. The atmosphere within a kiln during firing can affect the appearance of the finished wares. An oxidising atmosphere, produced by allowing air to enter the kiln, can cause the oxidation of clays and glazes. A reducing atmosphere, produced by limiting the flow of air into the kiln, can strip oxygen from the surface of clays and glazes. This can affect the appearance of the wares being fired for example, some glazes containing iron become brown in an oxidising atmosphere, but green in a reducing atmosphere. The atmosphere within a kiln can be adjusted to produce complex effects in glaze. Ceramic glaze is a glassy substance that coats the surface of a biscuit ceramic. In some phase, glaze content was melted to produce a glassy phase that infiltrated into the pores and covered biscuit body. Glaze is used to coats earthenware, stoneware and porcelain as glaze protects the diffusion of water or liquid into porous biscuit during operation. The glaze technique creates value for ceramics. The raw materials for glaze must include silica, which can be molten to be a glassy phase. Various metal oxides, such as sodium, potassium and calcium, act as a flux to reduce the melting temperature during glaze firing process [19]. The additional materials, such as iron oxide, copper carbonate and cobalt carbonate, are mixed in the glazing slip composition to obtain different color after glaze firing process. Another ancient pottery added alkaline into the glazing mixture. It was reported that the history of glaze firing process was generated at China. These products were recognized as stoneware and the porcelain. The specific Chinese pottery indicated that ash was added in glazing slip mixture. The glaze surface in ancient pottery of Ban Bo Suak was observed that glaze color was similar to ancient Chinese pottery. Therefore, it was believed that the ancient Ban Bo Suak pottery was influenced by Chinese pottery [20].

2.4 Ceramic Raw Materials

2.4.1 Clay minerals

Building ceramics accomplishes by firing natural clays which contains various materials. Kaolinite, the main constituent of kaolin, is formed by rock weathering. It is white, greyish-white, or slightly colored. Kaolinite is formed mainly by decomposition of feldspars (potassium feldspars), granite, and aluminium silicates. The process of kaolin formation is called kaolinization. Kaolinite is a hydrous aluminium silicate. It has a stable chemical structure and good physical properties for ceramic production. It is plastic, during drying phase the shrinkage is low, and its melting point is at 1750 °C [21]. Table 2.1 shows the classification of clay minerals. Crystalline species in small groups according to the type of bonding of a tetrahedron and octahedron [22]. Crystalline structure consisted of tetrahedral silicate sheets and octahedral hydroxide that could be classified as 1:1 or 2:1. For 1:1 clay structure, the structure has one tetrahedral sheet and one octahedral sheet, such as kaolinite and serpentine structures. Octahedral sheet is sandwiched between both tetrahedral sheets, such as talc, vermiculite and montmorillonite structures [23]. The classification of the phyllosilicate clay minerals is based collectively, on the features of layer type (1:1 or 2:1), the dioctahedral or trioctahedral character of the octahedral sheets, the magnitude of any net negative layer charge due to atomic substitutions, and the nature of the interlayer material (Figure 2.9, 2.10).

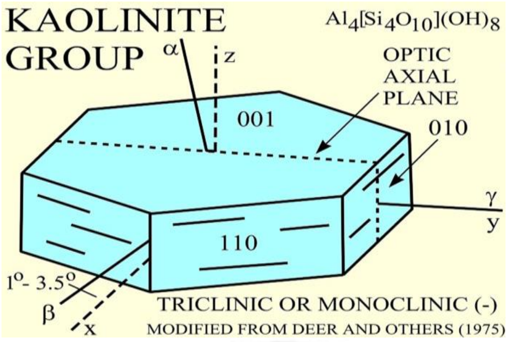


Figure 2.9 Basic units of kaolinite group [24]

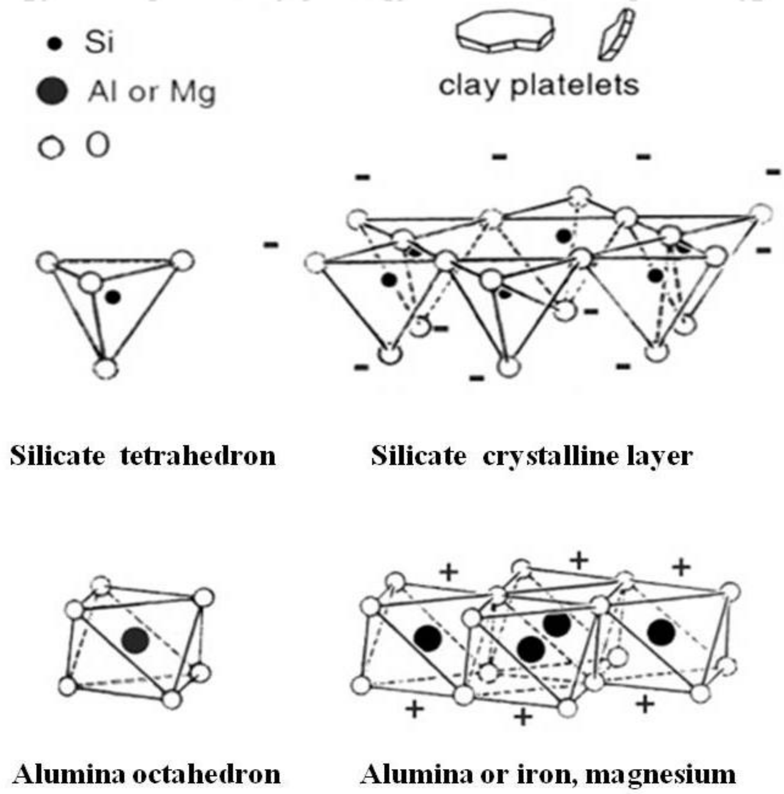
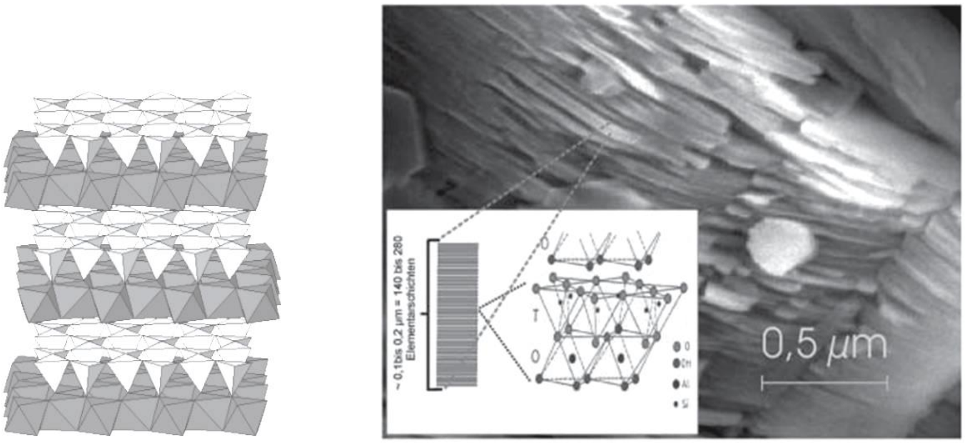


Figure 2.10 Basic units of clay minerals [24]

Kaolinite is the main constituent of kaolin. Its chemical structure is 39.8 % alumina, 46.3 % silica and 13.9 % water, which represents two-layer crystal (siliconoxygen tetrahedral layer joined to alumina octahedral layer exist alternately). The theoretical formula for kaolinite is $Si_2Al_2O_5(OH)_4$ (other formulas are $Al_2O_3.2SiO_2.2H_2O$ and $Al_2O_7Si_2.2H_2O$), which has a molecular weight of 258.071 g/mol. Kaolinite is build up from pseudo hexagonal triclinic crystals with diameter 0.2–10 μm, with thickness is 0.7 nm and its density is 2.6 g/cm^3. Kaolinite has a 1:1 sheet structure composed of SiO_4 tetrahedral sheets and Al (O, OH) 6 octahedral sheets [25]. The sheets are created from planes, which are occupied as follows: O6–Si_4–O_4– $(OH)_2$–Al_4 –$(OH)_6$. The morphology of the kaolin crystals is plate-like. The c-axis of the kaolinite crystal is perpendicular to the basal plane. Halloysite is a 1:1 aluminosilicate clay mineral with the empirical formula of $Al_2Si_2O_5(OH)_4$. Its main constituents are aluminium (20.90%), silicon (21.76%) and hydrogen (1.56%). Halloysite typically forms by hydrothermal alteration of alumino-silicate minerals. It can occur intermixed with dickite, kaolinite, montmorillonite and other clay minerals (Figure 2.11, 2.12).

Table 2.1 The classification of clay minerals [26].

General Distinction	Type	Expansion	Shape	Group	Minerals
Amorphous	-	-	-	Allophone	-
Crystalline	Two-layer	-	Equidimensional	Kaolinite	-
			Elongate	Halloysite	-
	Three-layer	Expanding	Equidimensional	Montmorillonite	Montmorillonite Sauconite,etc.
			Elongate	Montmorillonite	Nontromite Saponite Hectorite
		Non-expanding	-	Illite	-
	Regular Mixed-layer	-	-	Chlorite	-
	Chain structure	-	-	-	Attapulgite Sepiolite Palygorskite



(a) (b)

Figure 2.11 Kaolinite structure (a) the change of the tetrahedral (light) and Octahedral (dark) sheets, (b) structure of kaolinite [27].

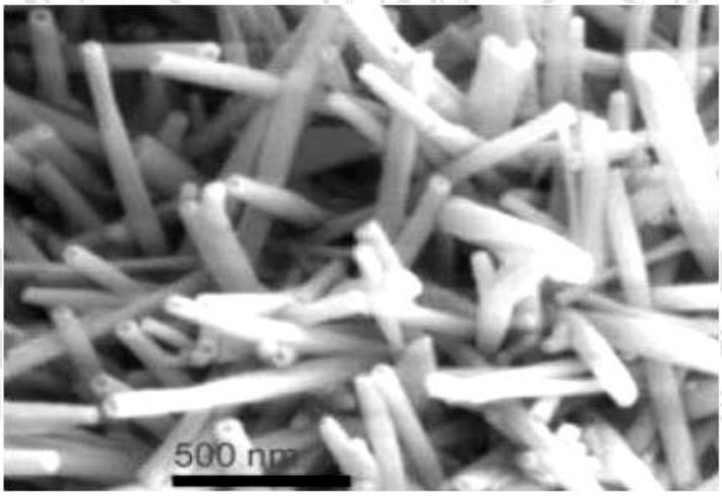


Figure 2.12 SEM micrograph of halloysite clay [28].

Clay mineral was the main material for ceramic production. It was formed due to slow disintegration of the stone. Clay minerals generally consisted of hydrated aluminum silicates. It should have fine crystalline size and usually found in plate or lamellar shapes. The chemical formula of this mineral was $Al_2O_3.2SiO_2.2H_2O$ or $Al_2Si_2O_5(OH)_4$ that was decomposed of the particularly feldspar, as shown in equation(2.2) [29].

$$\underset{\textbf{Feldspar}}{K_2O.\ Al_2O_3\ .6SiO_2} \xrightarrow[\substack{-\ K_2O \\ -\ 4SiO_2}]{+2H_2O} \underset{\textbf{Kaolinite}}{Al_2O_3.2SiO_2.2H_2O} \tag{2.2}$$

Kaolin clay had the series of phase transformations upon thermal treatment in air at atmospheric pressure. At 550-600 °C, hydroxyl (-OH) group began to separate from metakaolin ($Al_2Si_2O_7$) structure and this mechanism was called the endothermic dehydroxylation or dehydration. Dehydration loss continued until to 900 °C, where hydroxyl group in metakaolin ($Al_2Si_2O_5(OH)_4$) was completely eliminated to form kaolinite ($Al_2Si_2O_7$), as presented in equation (2.3) [30].

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2\ H_2O \tag{2.3}$$

Further firing at 925–950 °C, some SiO_2 was separated to form as α-quartz structure, while kaolinite structure was transformed as an aluminum-silicon spinel, $Si_3Al_4O_{12}$. This phase transformation is shown in equation (2.4).

$$2Al_2Si_2O_7 \rightarrow Si_3Al_4O_{12} + SiO_2 \tag{2.4}$$

Spinel phase was continually increased with higher firing temperature. It was then transformed to the mullite phase ($3Al_2O_3 \cdot 2SiO_2$) after firing at about 1050 °C, while α-quartz phase was slowly changed to cristobalite phase, as shown in equation (2.5).

$$3Si_3Al_4O_{12} \rightarrow 2\ Si_2Al_6O_{13} + 5\ SiO_2 \qquad (2.5)$$

Clay: Early potters used whatever clay was available to them in their geographic vicinity. However, the lowest quality common red clay was adequate for low-temperature fires used for the earliest pots. Clays tempered with sand, grit, crushed shell or crushed potteries were often used to make bonfire-fired ceramics. The coarser particles in the clay also acted to restrain shrinkage during drying, and hence reduce the risk of cracking. Traditional ceramics were produced from clay and combinations of clay and powdered or granulated non-plastic minerals. Traditional ceramics is often used to refer to ceramics in which the clay content exceed 20 percent and contained quartz sand [31]. Quartz or silica was essential constituents of granite and other igneous rocks. It was a combination of Si and O elements to form SiO_4 tetrahedral structure. Quartz could be transformed depending on the firing temperatures. At room temperature, it had stable structure of low quartz (α-Quartz). It was then transformed into high quartz (β-Quartz) after firing at 573ºC which was further transformed into hexagonal β-tridymite after firing at 867ºC. Final quartz structural phase was β-cristobalite phase, which was generated from the transformation of β-tridymite phase after firing at 1470ºC as show in equation (2.6) and reaction occurred during fired clay as shown in Figure 2.13 [32].

$$\alpha\text{-quartz} \xrightarrow{573\ ^{\circ}C} \beta\text{-quartz} \xrightarrow{867\ ^{\circ}C} \beta\text{-tridymite} \xrightarrow{1470\ ^{\circ}C} \beta\text{-cristobalite} \qquad (2.6)$$

High quartz content in clay caused reduction of the plasticity during forming process, while it could reduce drying shrinkage. Therefore, quartz must be added in clay that had high shrinkage to prevent cracking during firing process. During the vitrification period, it was combined with the basic oxides of the fluxing ingredients to form a glass which was responsible for the strength of the fired ware [33].

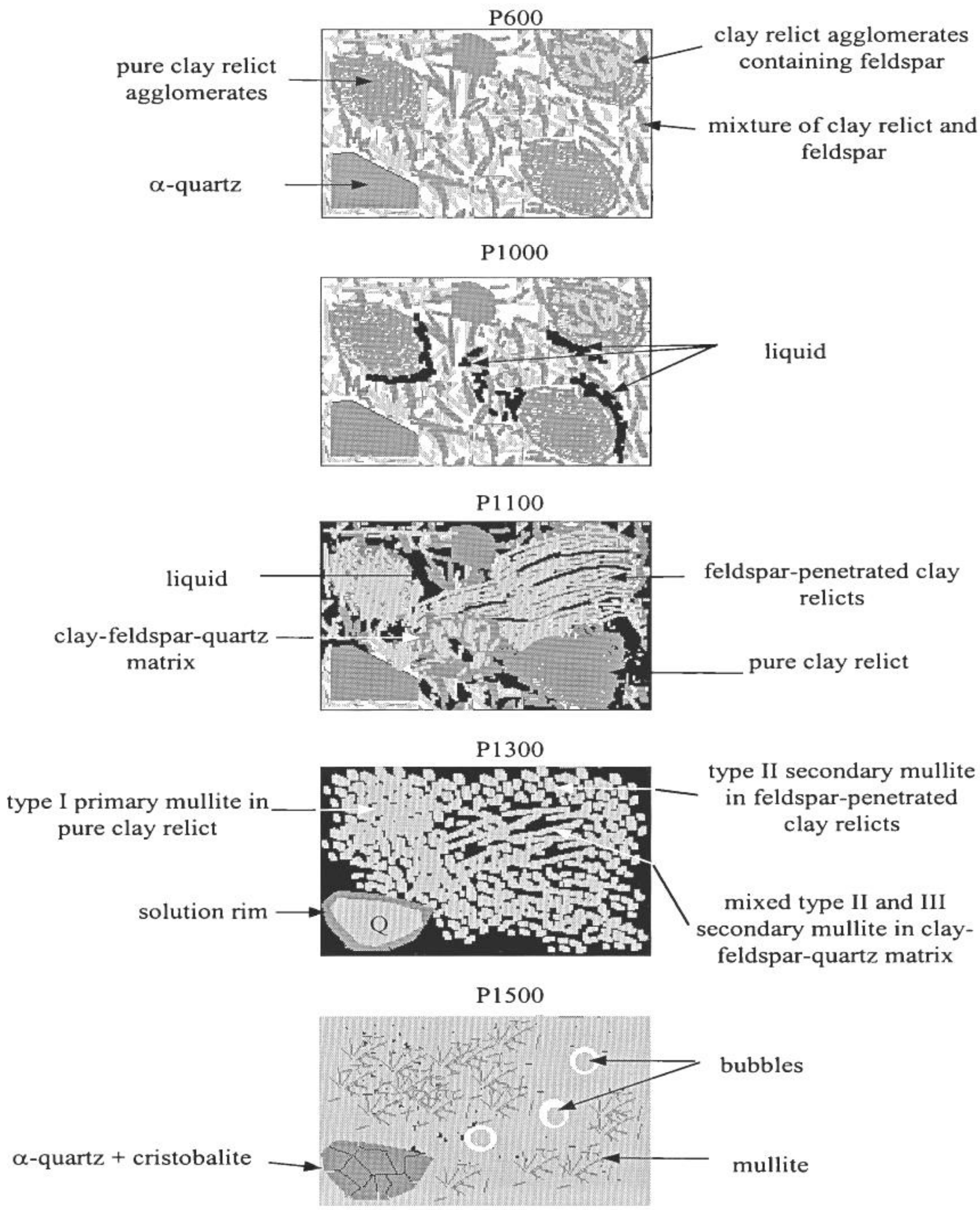


Figure 2.13 Microstructure evolutions in triaxial porcelain [34].

2.5 Preparation and analysis of ceramics

2.5.1 Plasticity

Although plasticity is a property that is essential to the usefulness of clays, it is the property which makes clays workable. A material like mud, or dough, or putty that can be formed readily by simple, moderate pressure, and which will retain whatever shape is thus imparted to it, is called plastic. To the potter, plasticity is practically the same as workability. It is commonly judged by the feel in the hands, or the way it behaves on the potter's wheel. But such methods are not capable of giving anything approaching a reliable measure of plasticity, and it is becoming increasingly important to measure this property so that the plasticity of a clay can be expressed as a definite, quantitative value. A considerable number of methods, some direct and others indirect, have been proposed for measuring plasticity, the indirect methods being based on the assumption that some other related but simpler and more easily measurable property would serve as an index to plasticity itself. The most noteworthy of the proposed indirect methods are those based on colloidal content, bonding power, and the so-called viscosity of the clay slip [35]. Clays exhibit many properties common to substances in the colloidal state, such as hydrolysis, absorption, shrinkage, ability to change from sol to gel form and vice versa. The colloidal theory is probably the most widely accepted explanation for the cause of plasticity, and the analogy between clays and substances in the colloidal state has led a number of investigators to look at the field of colloidal chemistry for a possible solution of the problem of measuring plasticity. Thus, assuming the plasticity of clay to be inversely proportional to the grain size, reasoned that the clay with the highest colloidal content would be the most plastic. In the study of clays for a number of industrial purposes, the determination of bonding power, which is the ability of clay to impart strength to a dried mixture made up in part of materials less plastic than itself, is extremely important. Thus, the plasticity developed by clays when mixed with water was unique. The effects of water on the physical properties of clay could be seen in the form of cracks. The amount of shrinkage of pure clay could be characterized using two laboratory variables: the ‘liquid limit’ and the ‘plastic limit’. The liquid limit is the point at which the water content was sufficient for the clay to flow as a liquid. The plastic limit was the moisture content at which the sample shears rather than remaining intact at this diameter. These data could be used to derive a plasticity index, which was simply the liquid limit minus the plastic limit [36]. This could then be plotted to show the potential for the clay to shrink, most clays fill close to the line shown in Figure 2.14. The effect of water on the physical properties of clay can be seen in the form of cracks in almost all contemporary and historical daub panels. It is also important that a daub, after any cracking, must have a residual strength in the clay that resists failure. Where a daub may be considered to have failed locally due to a crack or within its structure in the form of micro-cracks, the overall panel strength is assured by the added fibred such as straw or hair [37].

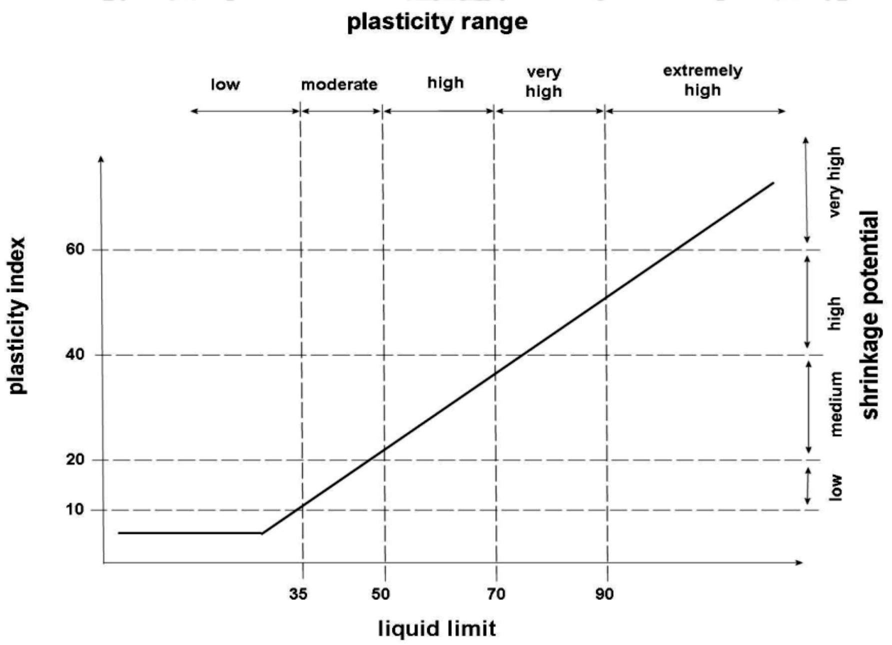


Figure 2.14 States of consistency and plasticity limits of clays [38].

2.5.2 Linear shrinkage

The Linear shrinkage test was an attractive alternative to the shrinkage limit test (ASTM D 427) which required determination of the final volume of the soil pat after oven drying [39]. The test only described the change in length of the sample even though three-dimensional shrinkage occurred. The three dimensional shrinkage was calculated by assuming that shrinkage was uniformed in all directions. The shrinkage occurred when a body or clay was dried from its normal plastic working consistency. This was called the wet-to-dry, dry-to-fired and wet-to-fired shrinkage of the material, and was usually expressed as a percentage of either the original wet length, or of the fired length. The shrinkage was easily measured by hand molding a block of the material at its working consistency in a plaster mold. A line was drawn and marks were made at some fixed distance a part 5 or 10 cm. A direct characterization of shrinkage could also be performed. This required measurement of the 'shrinkage limit', defined as the moisture content below which a clay ceased to shrink and the shrinkage ratio, which was defined in terms of the volumetric change versus change in moisture content [40]. The linear shrinkage was also particularly relevant to the cracking of daub panels. Figure 2.15 show a typical relationship between volume change and water content of clay. Below the shrinkage limit, air replaced the voids that had been filled with water. Above the shrinkage limit, the clay was called as being 'saturated' [41]. This meant that the voids were full of water and had displaced all the air. A dry daub was generally kept below the shrinkage limit, so contraction and expansion was negligible after the initial drying [42]. The shrinkage limit was determined by the following equation (2.7):

$$\% \text{ Linear drying shrinkage} = S_d = (L_p - L_d)/L_p * 100 \tag{2.7}$$

When: S_d = Linear drying shrinkage (%),

L_d = Dry length of test specimen,

L_p = Plastic length of test specimen

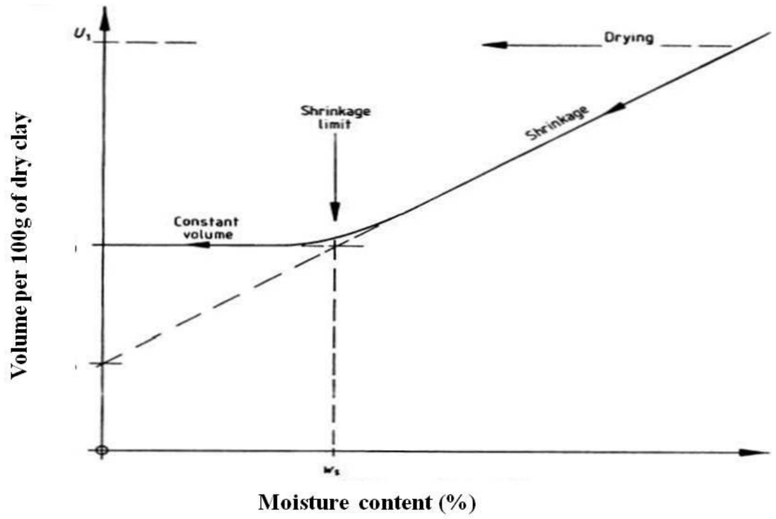


Figure 2.15 Clay moisture content versus volume [38].

2.5.3 Water absorption

Water absorption characteristics of porous pottery materials were of particular interest and practical significance. The total porosity of any masonry material had a determining influence on the compressive strength and also on the permeability of the material to water or liquid flow [43]. Water absorption was expressed as increase in weight percent as shown in equation: (2.8):

$$\text{Water absorption} = (W_3 - W_1)/W_1 \times 100 \tag{2.8}$$

When: W_1 = Weighed at dry state.

W_3 = Weighed again at the saturated wet state in air.

2.5.4 Bending strength

Bending strength testing was common in springs and brittle materials whose failure behaviors were linear such as concretes, glasses and ceramics. Bending test was therefore suitable for evaluating strength of brittle materials where interpretation of tensile test result of the same material was difficult due to breaking of specimens around specimen gripping. The evaluation of the tensile result was therefore not valid since the failed areas were not included in the specimen gauge length. For brittle materials having a liner stress-strain relation, the fracture stress could be determined from the fracture stress in bending according to a linear elastic beam analysis as shown in equation (2.9):

$$\text{Modulus of rupture (MOR)} = 3\,FL / (2bh^2) \tag{2.9}$$

The three point bending experimental procedure and example of bend testing under a three-point bend arrangement are shown in Figure 2.16. Bend testing was carried out using a universal testing machine until failure took place. Construct the load-extension or load-deflection curve if the dial gauge was used. Calculate the bend strength, yield strength and elastic modulus of the specimen [44].

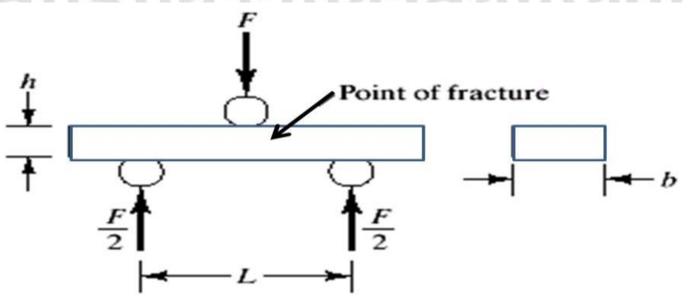


Figure 2.16 Example of bend testing under a three-point bend arrangement [44].

2.6 Sintering of ceramic

Sintering of ceramic materials is the method involving consolidation of ceramic powder particles by heating the “green” compact part to the temperature below the melting point, when materials of the separate particles are diffused to the neighboring powder particles. The driving force of sintering process is reduction of surface energy of the particles caused by decreasing their vapour-solid interfaces. During the diffusion process the pores, taking place in the “green compact”, diminish or even close up, resulting in densification of the part, improving its mechanical properties. Decrease of the porosity caused by the sintering process is determined by the level of the initial porosity of the “green” compact, sintering temperature and time [45]. Sintering is enhanced if the liquid phase takes part in the process. It defined as a process that takes place via phase transition and makes most bulk ceramic components compact [46]. Figure 2.17 shows ceramic sintering processes and Figure 2.18 shows stoneware body sintering at different temperature.

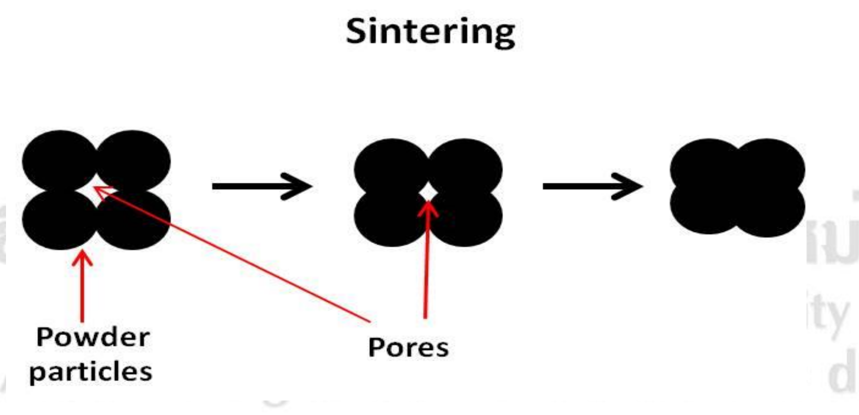


Figure 2.17 Ceramic sintering processes [47].

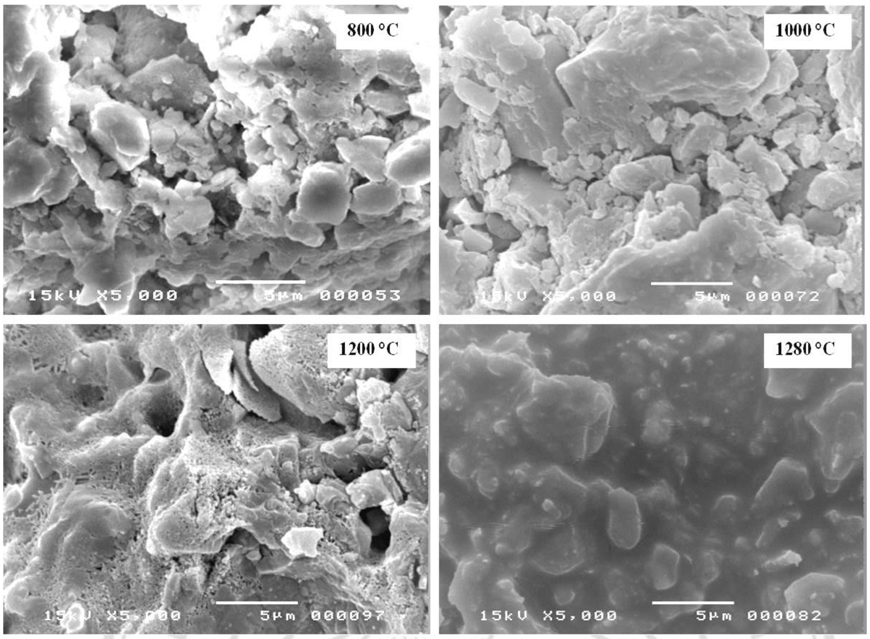


Figure 2.18 Example of sintering at different temperature.

Accordingly, sintering and phase decomposition in homogeneous ceramic matrix through firing have a significant use for determining the manufacturing process in ancient ceramics and, further-more, the quality of objects in the past. It is important to have an overview of the firing process. The changes in temperature make some profound changes in the clay [48]. The diagram of what happens to clay in the kiln is shown in Table 2.2. When pottery is placed into the kiln, it is almost always bone dry. However, there is still water trapped within the spaces between the clay particles. Wet clay contains large amount of water, a minimum of 25%, actually. When clay starts to dry, water evaporates from it. As this happens, the particles of clay are drawn closer together resulting in shrinkage. Sometimes these stress show up right away as cracks or warpage. These bodies shrink less because they have lower water content to start with, and also provide channels through which moisture can escape towards the surface. These are called “open” bodies. When the water evaporates from between the clay particles, and all the remaining clay particles are in contact, drying shrinkage is complete but the particles themselves are still damp. The formation of steam within the body of the clay may cause it to burst. For this reason, the early stages of firing clay are done slowly and with a peephole or lid open for steam to escape. The next change which occurs during the firing process is at about 350 °C, the point where the chemically combined water of the clay is driven off. This is water that is part of the molecular structure of the clay. This drying is completed at about 500 °C. After this point you can no longer mix dried clay with water to make new wet clay. An irreversible chemical change has taken place, known as dehydration. No shrinkage is observed during this stage. After dehydration, the next change that happens during the firing process is Quartz inversion, which happens at 573 °C. At this point, quartz crystals rearrange themselves into a slightly different order. A slight and temporary increase in volume occurs at this point. This is why you always need some space around pieces during firing, as they will expand somewhat. Firing should proceed slowly during this quartz inversion. A large percentage of ware that is cracked during the clay firing process happens from fast firing through this stage. The next stage that happens during the firing process is vitrification. This is the hardening, tightening and finally the partial classification of the clay. Vitrification results from fusions or melting of the various components of the clay. The strength of fired clay is increased by the formation of new crystalline growth within the clay body, particularly the growth of mullite crystals. Mullite is an aluminum silicate characterized by a long needlelike crystal. These lace the structure together, giving it cohesion and strength. Clays vitrify at various temperatures depending upon their composition. Red clay high in iron and other impurities might be fired to hardness at about 1000 °C and melt to liquid at 1250 °C. A kaolin body which is very free from impurities might not melt until over 1800 °C [49]. If you fire it high enough, the clay would first swell up (bloat) then fuse into a liquid which would cool as a glass. Of course in ceramics we don't fire that hot; we stop at the point where we have just enough fusion and hardness for durability, but not too much to cause deformation or melting of the ware. This point is called maturing of the clay [50].

Table 2.2 Reaction occurring on firing process [51]

Temperature (°C)	Reaction occurring on firing
	Reaction occurring on firing process
100	At this temperature, moisture left in the ware after drying and any hygroscopic moisture picked up from the atmosphere are driven off.
450-500	The clay mineral starts to decompose. Hydroxyl groups present in the clay structure are driven off as water in this reaction, which is known as dehydroxylation.
573	Quartz Inversion, A large percentage of ware that is cracked during the firing process. Firing slowly during this Quartz inversion.
900-950	Burn-off of carbon, sulfur and organic. Organic matters present in the body may burn off at 300-700 °C or even higher.
980	Sintering begins to occur. Temperature above about 900 °C vitrification, glass formation, may start.
1050-1100	New crystalline growth within the clay body, particularly the growth of mullite crystals.
1200	The strength of fired clay is increased by the formation of mullite.
1250	Clays sintering at 1250°C, vitrify at various temperatures depending upon their composition. The structure fuses into liquid which as a glass 60%, mullite 21 % and quartz 19%.

The sinter process is usually accompanied by other changes within the material such as chemical composition and crystal structure, distribution of pore size and shape in which some are desirable and some undesirable such as: pore and cracking defect. Figure 2.19 shows the liquid-phase sintering which generally regards as proceeding in a sequence of dominant stages: (1) melting of the liquid-forming additive and redistribution of liquid; (2) rearrangement of the majority of solid phases driven by capillary stress gradients; (3) densification and shape accommodation of the solid phase involving solution-precipitation; (4) final densification driven by residual porosity in the liquid phase [52].

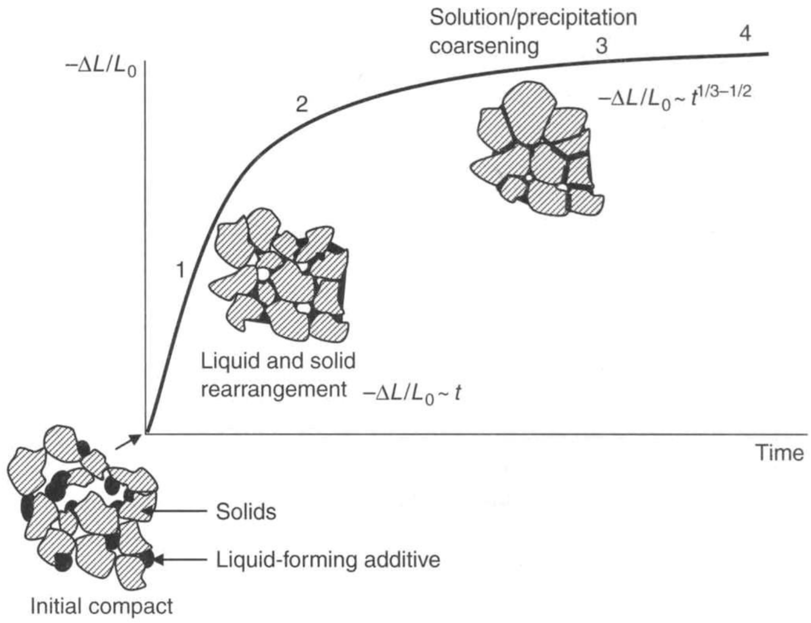


Figure 2.19 Schematic evolution of powder compact during liquid-phase sintering [52].

In many sintering processes, liquid phase is commonly used to enhance densification, lower the sintering temperature, achieve accelerated grain growth, or to produce specific grain boundary properties. In this case, a viscous glass or liquid present at the sintering temperature flows under the action of the capillary forces of the pores to fill up the porosity of the body. A relatively simple example of viscous sintering is that of a porous glass body (e.g., consolidated glass particles). A more complex example is the fabrication of clay-based ceramics (e.g., porcelain) from a mixture of naturally occurring raw materials. Chemical reaction, liquid formation, and viscous flow of the liquid into the pores lead to a dense body that on cooling consists of a microstructure of crystalline grains and glassy phases [53]. This rather complex case of viscous sintering in clay-based materials is referred to as vitrification (Figure 2.20**).**

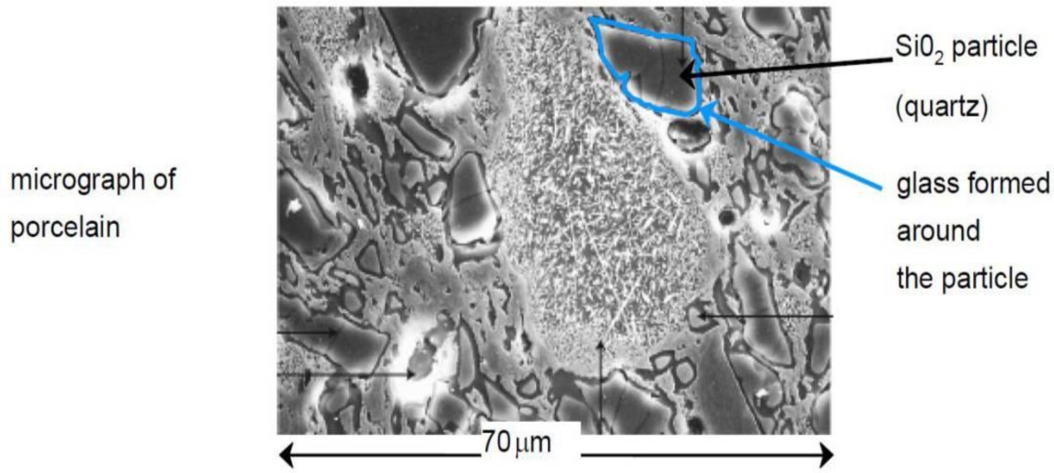


Figure 2.20 SEM shows liquid glass forms from clay and flows between SiO_2 flux melts at lower *T* [53].

The application of an external pressure enhances the densification rate in solidstate, liquid–phase, and viscous sintering. The chemical potential of the atoms under the contact surface (neck or grain boundary) is enhanced by the application of an external pressure, when compared to atoms under the pore surface, which leads to an increase in the driving force for densification [53].

2.7 Defect in Ceramics

Ceramics have interesting design properties. They have excellent mechanical properties in compression, but are terrible when tensile loads are applied to them, and are typically very brittle. The difference between the tensile and compressive performance of a ceramic is caused by the presence of preexisting cracks and flaws in the material. The presence of cracks and defects in the ceramic materials is called porosity. The porosity of a ceramic has a major effect on a ceramic's modulus of elasticity and modulus of rupture. Porosity of a ceramic is highly correlated with its mechanical properties, reducing the number of defects in a ceramic is a common way of increasing its strength. The most common way of lowering a ceramic's porosity is sintering; it was exposed to high temperatures. These temperatures depend on the material, but we should know that they will always be below the melting point of the ceramic. During the sintering process pores in the ceramic will close up [54]. The presence of small defects such as pores can lead to a drastic decrease in strength, elastic modulus, and fracture toughness [55]. After the ceramic matrix burning to find pore, caused by the melting and connecting incomplete. Common elements include quartz and glassy phase. Porosity was an important microstructure feature in most natural and man-made materials and often affected significantly on physical properties of these materials such as fluid permeability, shrinkage, density and yields rupture or ductile strength. The strength of the material is reduced significantly, when porosity increases [56]. Table 2.3 shows the strength of alumina with pore volume.

Table 2.3 Comparison effect of strength of alumina in content of pore [56].

Porosity (%)	Strength (MPa)
0	269
10	172
20	110
30	76
40	55
50	47

The other reason that leads to reduced strength is cracks defect. Ceramic deformation typically does not involve long-range deformation (i.e., deformation of all of the parts of the structure, but rather it entails very localized or short-range deformation. Before the mechanism of this process was understood, there was a great conundrum over the difference between theoretical strength and observed strength. Observed values were from 0.1% to 10% of theoretical values [57]. Alteration caused structural and volume modification with cracking of the external surface. Cracks increased the transport of fluids through the bulk of the glaze and favoured further alteration [58]. Griffith studied explained the process in terms of crack, flaws in ceramics produced crack. Crack tips propagating across a material only affect the local region of the crack tip [59]. This is called the Griffith-Orowan theory although all the parts of the process are now pretty well understood. Cracks are initiated at weak spots in ceramic materials (e.g., internal pores or external surface irregularities). Cracks are propagated by small stresses. Even water within the crack can propagate it. Ultimately cracks are terminated by being stopped or by crossing through the material to cause failure. This creates an external surface defect. Then flexing the pane away from the scratch creates tension and breaks the pane into pieces easily. The scratch is the crack initiator; the tensile stress is the crack propagator (Figure 2.21). Ceramics are weak in tension and strong in compression. Tensile forces encourage crack formation and propagation. Let’s look at a simple pore. A pore can exist in anything, but let’s consider a non-crystalline phase for the time being. Now assume that tensile stresses are being placed on the structure. The forces elongate the pore and cause a crack to form which is perpendicular to the tensile stress direction. Crack generation in tension:

- cracks are always perpendicular to the applied stress
- pores are most detrimental under tensile stress (not compression)
- water tends to propagate existing cracks in most materials

Crack propagation can occur because of stress around the crack or internal forces (e.g., water or other liquids within the crack) that create capillary pressures and push on the crack tip. The crack propagation can occur have tensile stresses tended to propagate crack tip and water or other observed liquids tend to open crack tip [60]. (Figure 2.22, 2.23).

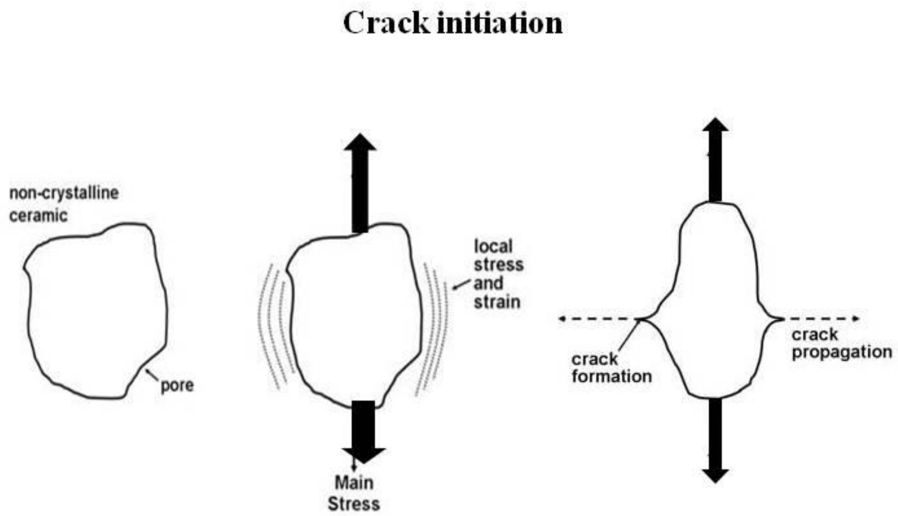


Figure 2.21 Crack initiations [58].

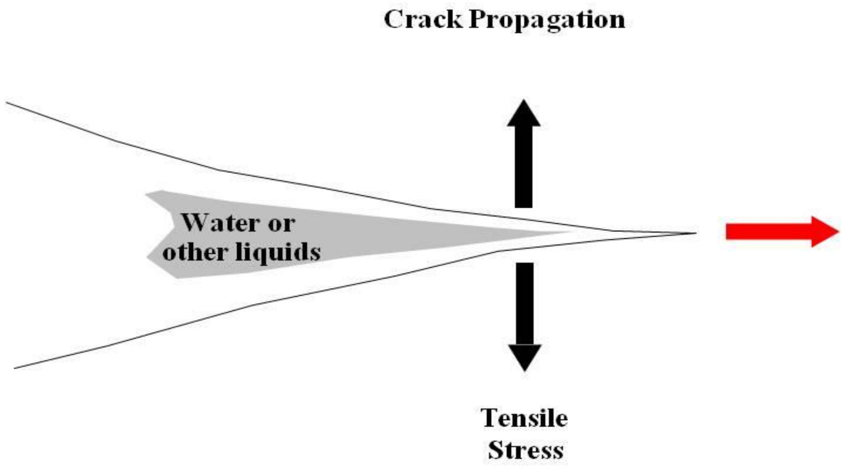
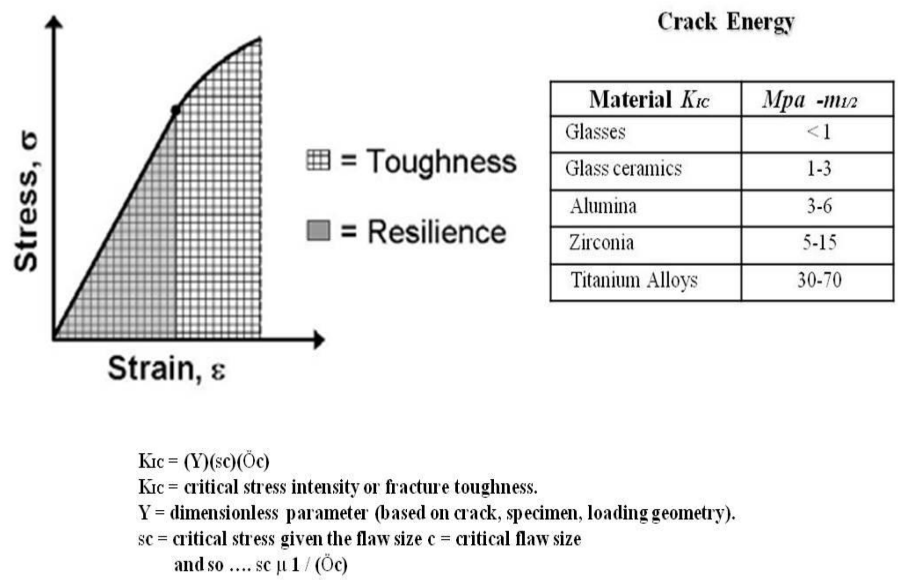


Figure 2.22 The crack propagation [58].



Material K_{IC}	Mpa -$m_{1/2}$
Glasses	< 1
Glass ceramics	1-3
Alumina	3-6
Zirconia	5-15
Titanium Alloys	30-70

Figure 2.23 The crack energy [58].

Consistent with the Fracture Mechanics, Griffith (1893-1963) began his pioneering studies of fracture in glass in the years just prior to 1920, he was aware of Inglis work in calculating the stress concentrations around elliptical holes and naturally considered how it might be used in developing a fundamental approach to predicting fracture strengths. However, the Inglis solution posed a mathematical difficulty: in the limit of a perfectly sharp crack, the stresses approached infinity at the crack tip. This is obviously nonphysical (actually the material generally underwent some local yielding to blunt the cracktip), and using such a result would predict that materials would have nearzero strength: even for very small applied loads, the stresses near crack tips would become infinite, and the bonds there would rupture, rather than focusing on the crack-tip stresses directly. A condition for crack growth was formulated. This equation also contained the influence of kinetic energy and continuum dissipation [61]. The stress required to create the new crack surface was given as follow equation fracture stress (σ_f) (2.10):

$$\sigma_f = \left[\frac{2E\gamma_i}{c}\right]^{1/2} \qquad (2.10)$$

σ_f = Fracture stress (Pa)

E = Young's modulus (Pa)

c = (Flaw size (m)

γ_i = Fracture energy for crack initiation (J/m^2)

Griffith equations explained the existence of defects or cracks at a micro level which were apparent available under normal condition, both on the surface and within the matrix. Tensile stress fracture occurred when the tip of the blame nib over the strength of the adhesion of the material. The rapid expansion cracks in the material had a low strength. After dehydration, the next change that happened during the firing process was quartz inversion, which happened at 573 °C. At this point, quartz crystals rearranged themselves into a slightly different order. A slight and temporary increase in volume occurs at this point. Firing should proceed slowly during this quartz inversion. A large percentage of ware that was cracked during the clay firing process happened from fast firing through this stage. Figure 2.24 showed the expansion cracks in the material with low strength, quartz shrinkage more than matrix (a) crack a circle line, if the matrix shrinkage more than quartz (b) a radial crack. The typical cracks observed around the quartz grains in the sample fired at 1050◦C and 1200◦C (Figure 2.25) [62].

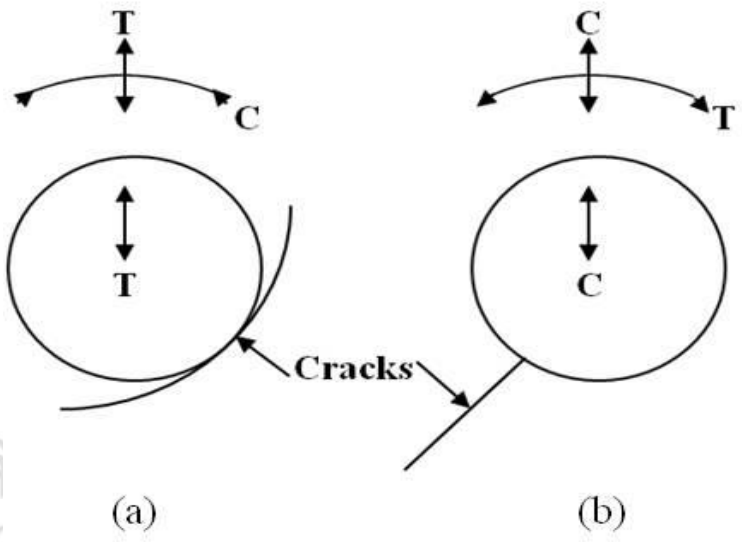


Figure 2.24 The expansion cracks in material (a) crack a circle line (b) a radial crack [62].

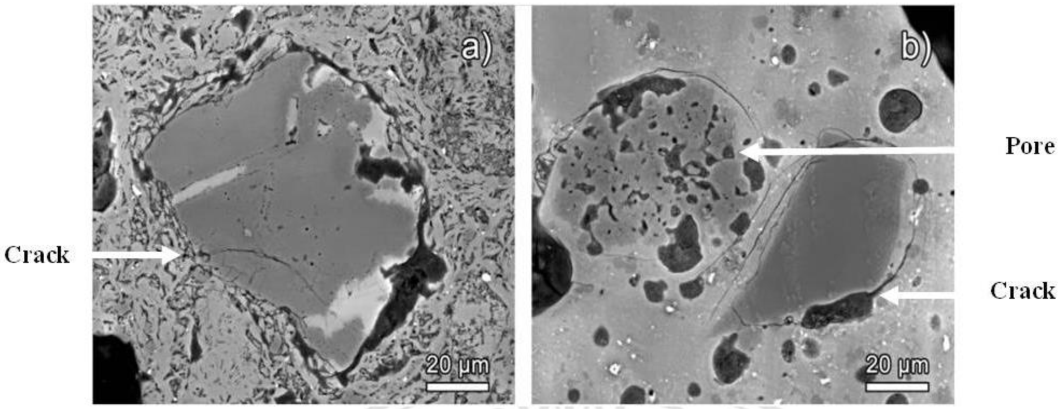


Figure 2.25 SEM micrograph showed typical cracks observed around the quartz grains in the sample fired up to (a) 1050°C and (b) 1200°C [63].

The ceramics hed test cracking in glaze; ASTM C424-93 (2012), Standard Test Method for Crazing Resistance of Fired Glazed Whitewares by Autoclave treatment[65]. This test method covered the determination of the resistance to crazing of fired, glazed, ceramic whitewares when stresses residual after glost firing might cause a tendency to craze, such stressed being induced by factors other than moisture expansion. All glazed might contain residual stresses from the firing that bonded the glaze to the body. In addition, ceramic wares have been increasingly subjected to thermal stresses in service. Hence, an important criterion used for glazing whiteware was adequate resistance to repeated abrupt thermal changes. In most cases, the result of inadequate resistance to thermal shock was the appearance of a craze pattern in the glaze. This craze pattern was visible by inspection with oblique lighting and application of a suitable ink or dye. This test method was applicable to vitreous whitewares that had negligible crazing as a result of moisture expansion [64]. For nonvitreous and semivitreous bodies, refer to ASTM Test Method C424-93. Test Method C424-93 covered a method for determining resistance to crazing induced by moisture expansion. Its use was generally confined to testing nonvitreous and semivitreous ceramic whitewares because these products might be subject to such expansion (Table 2.4).

Table 2.4 ASTM Standards C424-93 Test method for crazing resistance of fired glaze whitewares by Autoclave treatment [65].

Time (hour)	Body and Glaze resistant (year)
1	1-2
2	2-3
3	4-6
4	9-10
5	13-15

A research studied on the cracking defect as follows: strength of various glasses, with a range of expansion coefficients, containing 10 vol. % theories spheres, stresses occurred around the spheres, due to differences in the expansion coefficients of the glass and the spheres, on cooling from the fabrication temperature. An approximate value for the critical diameter might be obtained by an energy balance criterion. Cracks might form around spheres smaller than the critical diameter under application of applied stress at stresses below the macroscopic fracture stress. In these cases the strength was governed by a Griffith relationship with the crack size equal to the sphere diameter. When the expansion coefficients of the spheres and glass were similar, the strength of the glass was reduced only when large spheres are present [62]. The factors affecting results of strength divided into two factors, the first factor believe that the strength was based on the mechanism of crack microns (Micro crack) caused by expansion of unequal heat between particles. Quartz glasses with a matrix of factors were controlled by two large cracks particles of quartz [66]. The changes were the result of changes in volume and rupture of the surface. This caused cracks to increase the penetration of liquid into the coating [67].

2.8 Deterioration of Ceramics

Archaeological objects made of stone or fired clay were exposed to a number of processes, mechanisms and causes of decay; some were closely related to the intrinsic properties and nature of the materials, such as their mineralogy and texture (pores and cracks). While, others were induced by outside agents such as microclimate, environmental pollution or the anthropogenic or natural surrounding environment (air, water and soil). This type of decay has been less thoroughly analyzed in archaeological ceramics, despite the abundance and variety of such materials found at archaeological sites. Ceramics were created from a production of coatings of inorganic, nonmetallic materials using heating and cooling to create a glaze. Typically the coatings were permanent and sustainable for utilitarian and decorative purposes. General treatment of ceramics was consistent with that of glass because they were made of similar oxygen-rich components such as silicates [68]. Ceramics could be broken down into three groups: unfired clay, earthenware or terracotta, and stoneware and porcelain. It was the nature of all materials to eventually degrade and deteriorate. Degradation of the objects occurred from interaction with the environment or with the materials that form the object however, in the case of ceramics, environmental factor were the major factor. There were several ways in which ceramics broke down physically and chemically. Additionally the type of ceramic would affect how it broke down. Unfired clay, like mud and clay adobe was clay that was fired less than 1000 °C. This type of clay was water soluble and unstable. Earthenware was clay that had been fired between 1000-1200 °C. The firing made the clay water insoluble but did not allow the formation of an extensive glassy or vitreous within the body. However the materials also created a very brittle surface which increased the potential for chips, cracks and breaks.

Degradation of ceramics:

1. Physical Degradation: Due to their fragility, damage to ceramics typically came from mishandling and packing. However, other factors such as vandalism, frost, mold and other similar occurrences could also inflect harm.

2. Chemical Degradation: Chemical decomposition. Chemical degradation of objects occurred not in the physical structure of the object but rather in at the chemical or compound level. Compounds began to breakdown into simpler compounds and were often an undesired reaction. The degradation of the chemical component of an object would hinder or weaken the stability of the object when exposed to environmental factors such as water, air, pollution, heat, humidity and the like. Water could dissolve or deform ceramics that had been low fired, i.e. temperatures around 600 °C. Ceramic fired in high temperatures might also be susceptible to water if their mineral particles were soluble, for example gypsum or calcite. Additionally the different compounds in water could flux and react differently to different ceramics. In naturally occurring water, carbon dioxide was dissolved and could create a chemical reaction with minerals in clay bodies that might form calcium bicarbonate which is very soluble. Stagnant water was less damaging because the carbon dioxide was not exhausted [69]. Soluble Salts: A common degradation issue in ceramics involved soluble salts. Soluble salts could either enter the clay body from the environment, for example from being buried underground for decades, or they were already naturally occurring due to the components of the materials or clay used. Non-archaeological objects, such as modern dishware, could acquire salts from normal use such as storing salt. Soluble salts responded to changes in humidity both high and low. In high humidity salts became soluble and in low humidity they crystallized. The changing from soluble to crystallization and back damaged the surface of the ceramic because salt crystals were larger than liquid salt and therefore would shrink and expand the ceramic body [70]. A white haze on the surface was the first indication of soluble salts, which was the salt crystallizing. Overtime the physical component of the body would crumble until it was completely destroyed [71]. This procedure was done as the objective comparison of the degradation accelerated in laboratory to the alteration of the material under local environmental conditions. Samples were exposed to periods of 6, 8 and 10 months where variables like air temperature, relative humidity, wind speed, precipitation and the solar radiation, were recorded. This kind of degradation was used for long time prediction which would serve as a base to obtain the information about the effects of the degradation of a

specific material. Most of ceramic materials were fragile and stiff, with very low tenacity. Despite its stable mechanical behavior, it was not rare to observe problems in ceramic bodies regarding its durability, i.e., strength against weathering. Cracks and weathering signs were well developed inside the ceramic body, with time, due to work done by external agents like temperature and humidity [72]. The example of main problem found in construction materials regarding their durability were:

1. Deterioration in brick wall and tiles resulting in cracks and infiltration.

2. Degradation of the first lines of masonry due to capillarity effect of sulphate water (NA_2SO_4).

3. Rapid degradation due to sudden change in temperature.

4. Quickly degradation in coastal environment resulting in complete deterioration of the ceramic brick.

Chemical agents could flow into these cracks and pores, reducing, thus, the bond between grains, making erosion process easier and leaching the constituent materials. These transported constituents could induce the formation of new crystals resulting from chemical reactions, mainly when soluble salts were present in the mortar. When the humidity penetrated into the structure, these crystals were generally dissolved and carried to the surface, provoking thus and stains on the ceramic artifact. If these salts remained inside the ceramic body, they would re-crystallize causing expansion, favoring thus, degradation of the material. The intensity of the effects of these degradation processes was closely dependent on the environmental conditions and also on the level of the thermal treatment specified to the ceramic material. Degradation process of tiles in the step Pyramid at Saqqara, the study found that cross section in samples faience tiles showed that the components of faience tiles were mixture of crushed quartz or sand which with small amount of lime. The quartz appeared as angular grains and would see the pores and cracks in the body matrix which appeared in black color. All previous deterioration factors resulted in high moisture in the walls, salt crystallization and finally human negligence of the maintenance [73]. The deterioration of building ceramics, mainly glazed roof tiles of the Museum of Applied Arts. Identified residues of former biological activity, confirmed also by the presence of calcium oxalate. It was demonstrated that in some tiles the glaze had started to weather. If the phenomenon continued for a long period, it will be result in the deterioration of glaze [74]. Archaeological pottery made of stone or fired clay were exposed to a number of processes, mechanisms and causes of decay; some were closely related to the intrinsic properties and nature of the materials, such as their mineralogy and texture (pores and cracks), while others were induced by outside agents such as natural surrounding environment (air, water and soil. This study showed that both soluble salts absorption and their elimination after the desalination procedure was closely related to ceramic firing temperature and hence to the surface area and porosity generated during firing [75].

The magnesium sulfate salts and historic building materials: experimental simulation of limestone flaking by relative humidity cycling and crystallization of salts. Magnesium sulfate salts often resulted from the combination of incompatible construction materials, such as stone or mortar with high magnesium content and sulfates from adjacent mortars or polluted air. Damage by flaking took place in two types of magnesium limestone cubes impregnated with the salt mixture, apparently by deliquescent salts of low equilibrium relative humidity, while the rest of the samples developed a salt crust over the surface [76].