

# Characterisation of Vieng Kalong Clays and Relation between Physical Properties and Bloating

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**ABSTRACT:** This research aimed to study physical properties of two ball clays received from Ban Tung (TC) and Ban Rong (RC), Tambol Vieng Kalong, Chiang Rai, Thailand, and also to identify the key factors that affect the quality of the ceramic wares made from these clays. X-ray diffraction (XRD) and X-ray fluorescence (XRF) results revealed that RC clay contained higher free quartz content, while TC clay contained higher flux minerals. TC clay exhibited higher drying and firing shrinkage but lower water absorption after firing at 1250 °C. After firing at 1200 °C and 1250 °C TC, clay was subjected to warping and exhibited lower bending strength than RC clay due to bubble defects or bloating evenly distributed both inside the clay body and on the surface. EDX analysis showed that the defect areas contained a very high level of potassium, suggesting that they were initially coarse microcline particles. When TC clay was pretreated by ball-milling, the defects disappeared and the bending strength was significantly improved.

**KEYWORDS:** Clay, Defects, Strength, Vitrification.

## INTRODUCTION

Vieng Kalong was situated in the old northern Thai kingdom of Lan Na around 700 years ago. It was famous for manufacturing stonewares, both glazed and unglazed, which were white, fine and thin potting. This area was an ideal ceramic manufacturing center due to the availability of indigenous high quality clay mineral that is high in kaolinite and sufficiently plastic to throw. From the archeological evidence, fine ceramics in the old northern Thai kingdom of Lan Na were not manufactured before the consolidation of the country at the end of the 13<sup>th</sup> century. It is thus possible that the fine ceramics of Vieng Kalong were produced from the 14<sup>th</sup> century until the middle of 16<sup>th</sup> century<sup>1</sup>.

Presently, indigenous clays from Vieng Kalong are still used to produce ancient-style wares by a number of local potters. Although they were formed by the same throwing technique, the ancient pots are apparently whiter, lighter, and thinner. Besides, in some cases, duplicated wares exhibited relatively poor mechanical properties, which could be related to the presence of defects such as cracks and bloating observed on the surfaces.

The initial mix of clay bodies contained relatively large grains of quartz and feldspar in a matrix of finer clay particles. Clay particles provided plasticity and green strength during forming. Quartz acted as filler whose coarse grains provided resistance to cracking during drying and to reduce distortion and shrinkage

during firing. Feldspar provided fluxing actions, which led to densification in the presence of a reactive liquid phase<sup>2</sup>. Vitrification behavior and mechanisms of clays were reported to be governed by types, contents, and particle size of the main constituent minerals<sup>3-8</sup>. In general it was reported that dehydroxylation of kaolinite occurred around 550 °C and resulted in formation of metakaolin, which transformed to spinel and amorphous silica at around 1000 °C. At temperature above 1100 °C, the spinel transformed to silica and aggregate of small crystals (<0.5 μm) of primary mullite. Secondary mullite crystals, which appeared as long needles, were formed by the reaction of clay relicts with feldspar relicts at around 1200 °C<sup>6</sup>.

Mechanical properties of triaxial bodies were reported to be affected by many factors. Three hypotheses, namely the mullite hypothesis, the dispersion strengthening hypothesis and the matrix reinforcement hypothesis have been proposed to explain the mechanical properties of ceramic bodies<sup>9</sup>. However, there are still some research results which do not fit well with the proposed theories. Some groups reported the detrimental effect of residual quartz to the mechanical properties<sup>10-11</sup>. Grain size of quartz was also reported to have a significant effect on the mechanical properties, while the most proper grain size was still of argument<sup>12-13</sup>.

From the statements above, the factors governing the physical properties of triaxial bodies are still of debate. Besides, physical properties of unmodified

natural clay have not been widely studied. This research therefore aimed to study the basic properties of indigenous clays from Vieng Kalong, which are presently used for ceramic production and also to identify the key factors that affect the quality of the wares. This research was carried out in order to make the most benefit of natural resource utilization.

## MATERIALS AND METHODS

The clay samples, coded as TC and RC respectively, were received from Ban Tung and Ban Rong, Tambol Vieng Kalong, Chiang Rai Province, Thailand. Lumps of the clay samples were crushed and sieved through a 35-mesh stainless steel sieve, then dried in an oven pre-set at 110°C for 3 hours prior to characterisation. Chemical analysis was performed using an energy-dispersive X-ray fluorescence spectrometer (Horiba, Japan), while phase analysis was performed using an X-ray fluorescence diffractometer (X'pert Pro MPD, Philips, Netherlands). Average particle size and particle size distribution of the clay samples were measured using a laser diffraction technique (Mastersizer2000, Marlvern, UK). Thermal analysis, which was performed using a TGA/SDTA 851e STARE thermobalance [Mettler Toledo, Switzerland]. For physical property testing, the sieved clay was thoroughly mixed with water at a weight ratio of 70 to 30, and pressed in a plaster mold to obtain rectangular bars with the dimensions of 12 cm×2 cm×1 cm. The bars were dried in an oven pre-set at 110 °C for 24 hours, prior to firing at 800 °C, 1,000 °C, 1,200 °C and 1,250 °C. Bulk density values were calculated from the weight and the geometric volume of the bars after drying or firing. The mean density values were averaged from 10 samples. The drying and firing shrinkage were calculated. Water absorption values of the fired samples were determined using water immersion technique based on the Archimedes method. Refractoriness of the clays was determined by firing the bar samples in an electric furnace at 1,200 °C, 1,250 °C and 1,280 °C, and the sagging distance of the fired bar was measured.

Green and fired strength measurements were determined by three point bending technique using a Universal Testing Machine [Instron 2000, UK]. The span width of 8 cm and the crosshead speed of 5 mm/minute were chosen for all measurements. The fracture strength in kg/cm<sup>2</sup> was calculated as follows;

$$\text{Strength} = \frac{3LD}{2WT^2} \quad (1)$$

Where L is the breaking load in kg, D the span width in cm, and W and T are the width and the thickness of the bar samples in cm, respectively.

Phase development of the clays in the fired samples

was observed using an X-ray Diffractometer (X'pert Pro MPD, Philips, Netherlands). Fractured surfaces of the fired bars were examined using a scanning electronmicroscope (SEM) (LEO 1450 VP, Zeiss). The defect areas were investigated using the SEM attached with an EDAX-EDS.

## RESULTS

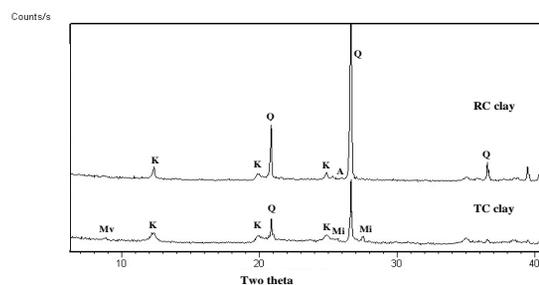
### Chemical and Phase Analysis

Chemical compositions of the clay samples obtained from energy-dispersive X-ray fluorescence (EDXRF) analysis is shown in Table 1. RC clay contained a relatively high SiO<sub>2</sub> but a rather low alkaline, while TC clay exhibited an opposite trend. Al<sub>2</sub>O<sub>3</sub> content was higher in TC clay than RC clay. While Fe<sub>2</sub>O<sub>3</sub> content was relatively similar in both clays, TiO<sub>2</sub> content was higher in RC clay.

**Table 1.** Chemical analysis of the clays obtained from Vieng Kalong district.

Clay	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	L.O.I.*
TC	63.46	24.19	2.50	0.26	1.43	0.75	7.41
RC	75.17	17.06	0.81	0.44	1.32	1.43	3.77

\*L.O.I. at 1000 °C was obtained using TGA.



**Fig 1.** XRD results of Vieng Kalong unfired clay with indications of constituent minerals. K: kaolinite, Q: quartz, Mv: muscovite, Mi: microcline, A: anatase.

The XRD analysis of the clays are shown in Fig. 1. Constituent minerals were identified from the obtained XRD patterns using the method described by Dorothy<sup>14</sup>. The results showed that the main minerals in both clays were kaolinite, quartz, and microcline, while muscovite and anatase were found only in RC clay. Comparatively, the content of free quartz in RC clay was distinctively higher than TC clay. Quantitative analysis results of the constituent minerals were reported elsewhere<sup>15</sup>. Peak broadening at the 2θ-angle of 12.5° in TC clay could be due to either the smaller crystal size<sup>16</sup> or the lower degree of crystallization of kaolinite crystals<sup>17</sup>. However, the analysis result in Section 3.2 showed that the particle size distribution and also the mean particle size of both

clays were very similar. It was thus believed that the lower degree of crystallization was likely accounted for the broadening of kaolinite peak in TC clay.

### Particle Size Analysis

Particle size analysis result showed that both TC and RC clays had relatively similar particle size distribution curves. The average particle size of TC clay was 10.1  $\mu\text{m}$  while that of RC clay was 11.0  $\mu\text{m}$ . Particle size distribution played an important role in packing of the particles, while the particle size had a significant effect on vitrification rate of the clays. However, other factors such as quartz and feldspar contents are also of importance to the thermal behavior of the clays and must also be considered.

### Thermogravimetric Analysis

The thermogravimetric analysis showed that both clays exhibited a similar decomposition curve, i.e. starting and ending around 100 °C and 700 °C, respectively, but with different percentages of weight loss. A dramatic weight loss in the temperature range of 300-700°C was due to an oxidation of organic matters and a change of crystal structure from kaolinite to metakaolin accompanied by the loss of crystallised water. TC clay exhibited higher total weight loss of approximately 8% while that of RC clay was about 5%. This result was expected since TC clay contained a higher clay-to-quartz ratio than RC clay, and therefore lost more water during the dehydroxylation reaction.

### Physical Properties

#### Drying and Firing Shrinkage

Drying and firing shrinkage results of the clays are listed in Table 2. The higher drying and firing shrinkage of TC clay could be due to a higher clay-to-quartz ratio and a higher content of fluxing minerals in this clay than RC clay. In addition, the lower degree of

crystallization of kaolinite in TC clay might also contribute to such higher drying shrinkage compared with RC clay. In contrast, a higher quartz content in RC clay could be responsible for its lower shrinkage at all temperature ranges compared with TC clay.

#### Green Density and Water Absorption

Green density and water absorption of TC and RC clay samples fired at different temperatures are shown in Table 3. After firing at 800 °C and 1000 °C, water absorption of the TC clay samples (~20%) were higher than that of the RC clay samples (~14%). This might be associated with the higher organic content as well as the higher clay-to-quartz ratio in TC clay than RC clay. The initial mix of the green body contained relatively large crystals of quartz and feldspar between which were the matrix of finer clay particles. Phase analysis of RC clay showed a lower clay-to-quartz ratio which led to better particle packing, higher green density and thus lower water absorption in the RC clay samples fired at 800 and 1000°C compared with TC clay. Loss of crystallised water and organic matters in both clays had occurred below 800°C, causing an increase in porosity of the body. Such pores in the bodies must be eliminated upon firing to obtain vitreous bodies. Rapid decreases in water absorption value of TC clay samples after firing at 1200-1250 °C indicated that this clay started to vitrify at 1200°C due to the higher flux content, while RC clay samples were relatively porous at this temperature range.

#### Refractoriness

Refractoriness of the clays was measured as sagging distance of the bar samples. The results indicated that RC clay was considerably more refractory than TC clay. RC clay samples can be fired up to 1250 °C without any warping while TC clay samples considerably sagged at this temperature. Warping of TC clay samples was due

**Table 2.** Drying and firing shrinkage of Vieng Kalong clays as a function of firing temperature.

Clay Sample	As dried	Shrinkage (%)			
		As fired (°C)			
		800	1000	1200	1250
TC	6.20 $\pm$ 0.27	6.70 $\pm$ 0.27	8.00 $\pm$ 0.35	14.30 $\pm$ 0.57	14.70 $\pm$ 0.97
RC	3.80 $\pm$ 0.27	4.40 $\pm$ 0.42	4.50 $\pm$ 0.35	7.40 $\pm$ 0.22	7.80 $\pm$ 0.27

**Table 3.** Green density and Water absorption of Vieng Kalong clays fired at different temperatures.

Clay Sample	Green density(g/cm <sup>3</sup> )	Water Absorption (%)			
		800°C	1000°C	1200°C	1250°C
TC	1.73 $\pm$ 0.05	20.36 $\pm$ 0.33	20.23 $\pm$ 0.43	5.40 $\pm$ 0.33	2.80 $\pm$ 0.49
RC	1.83 $\pm$ 0.03	14.18 $\pm$ 0.36	14.49 $\pm$ 0.42	9.63 $\pm$ 0.14	8.29 $\pm$ 0.30

**Table 4.** Bending strength of the clay samples after drying and firing at different temperatures.

Clay Sample	Bending strength (Kg/cm <sup>2</sup> )				
	As dried	As fired (°C)			
		800	1000	1200	1250
TC	32.70 ±2.68	65.67 ±5.74	103.02 ±4.92	170.16 ±10.04	196.96 ±13.33
RC	42.61 ±4.90	47.42 ±3.31	82.96 ±6.31	218.70 ±4.30	240.56 ±16.60

to the high flux content in this clay that lowered its hot strength and thus the resistance to warping. In contrast, RC clay contained a higher content of quartz which made it more resistant to warping than TC clay.

### Bending Strength

Bending strength values for the samples are shown in Table 4. Green strength of the TC clay samples was slightly lower than that of the RC clay samples. After firing at 800 °C, the bending strength of the RC clay samples only slightly increased while that of the TC clay samples greatly increased. At the firing temperature of 1000 °C and above, the bending strength of both clays steadily increased. At 1200 °C and 1250 °C, the bending

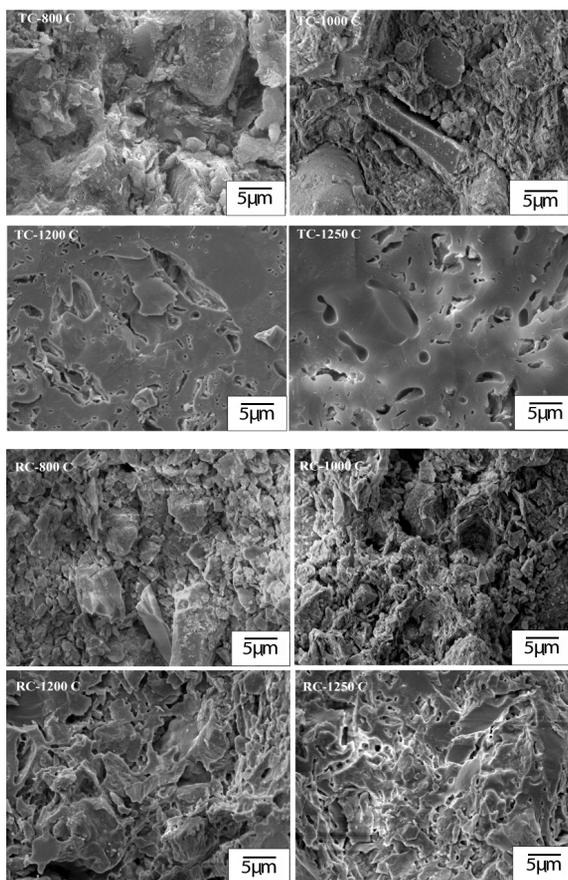
strength of the TC clay samples became inferior to that of the RC clay samples. From literatures, strength of ceramic bodies could be affected by many factors such as degree of vitrification, mullite needle interlocking, grain size of the minerals glassy phase and residual quartz content as well as defects occurred in the body<sup>18-21</sup>. Grimshaw stated that when the clay contained too many fine clay particles or it was over-fired, excessive shrinkage and warping distortion could occur. This led to loss of strength<sup>18</sup>. The warping distortion of TC bars and their inferior bending strength was believed to be due to one of the reasons stated above. Besides, microstructure observation (Figs. 2 and 3) showed that this clay, after firing at 1250 °C, had a large number of defects both on the surface (bloating) and inside the body. These defects were filled with bubbles which could deteriorate the strength of the clay samples.

### Phase Changes upon Firing

Phase change of TC and RC clays after firing at 800-1250 °C are relatively similar. The disappearance of kaolinite peaks in both clay samples fired at 800 °C and above was due to the kaolinite-to-metakaolin transformation around 550 °C<sup>2</sup>. Microcline was still observable in the TC clay samples fired at 1000-1200 °C, while muscovite had disappeared since 800 °C. At 1200 °C, mullite phase was first observed with some residual quartz. Further increase of firing temperature did not make much change. The RC clay samples fired at 800 °C showed existence of neither kaolinite nor microcline. Two new phases, cristobalite and mullite, were found in the samples fired at 1200 °C. After firing at 1250 °C, there existed three phases: mullite, cristobalite and quartz, in which the quartz content was much higher than that of TC clay.

### SEM Micrographs

SEM micrographs taken from fractured surfaces of TC and RC clay samples fired at 800-1250 °C are shown in Fig. 2. At firing temperature of 800-1000 °C, glassy phase was not observed in both clays suggesting that vitrification had not yet occurred at these temperature ranges. At 1200 °C, the morphology of TC clay suggested the presence of the glassy phase and thus vitrified body. RC clay, however, was still relatively porous at this firing temperature. At 1250 °C, TC clay still showed higher degree of vitrification than RC clay. This evidence was



**Fig 2.** Comparative SEM micrographs for the fired TC (upper) and RC (lower) clay samples.

in good agreement with the water absorption measurement and refractoriness testing results.

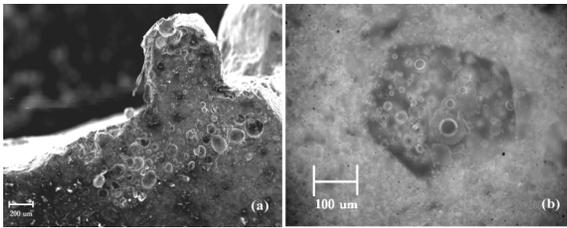
**Analysis of the Defect and its Effect on the Strength**

After firing at 1250 °C, a large number of bubble defects or more specifically bloating which were around 500 μm in diameter appeared on the TC clay sample surface. SEM micrographs taken from the cross-section of a surface eruption area showed that the defect was not only originated from the surface but also from the body (Fig. 3(a)). In fact, an optical micrograph of a specimen cross-section area in Fig 3(b) showed that the TC samples contained a large number of similar air bubble pockets. Such trapped air pockets in the ceramic bodies could arise due to a number of reasons such as over firing, too rapid firing, or the increase in the content

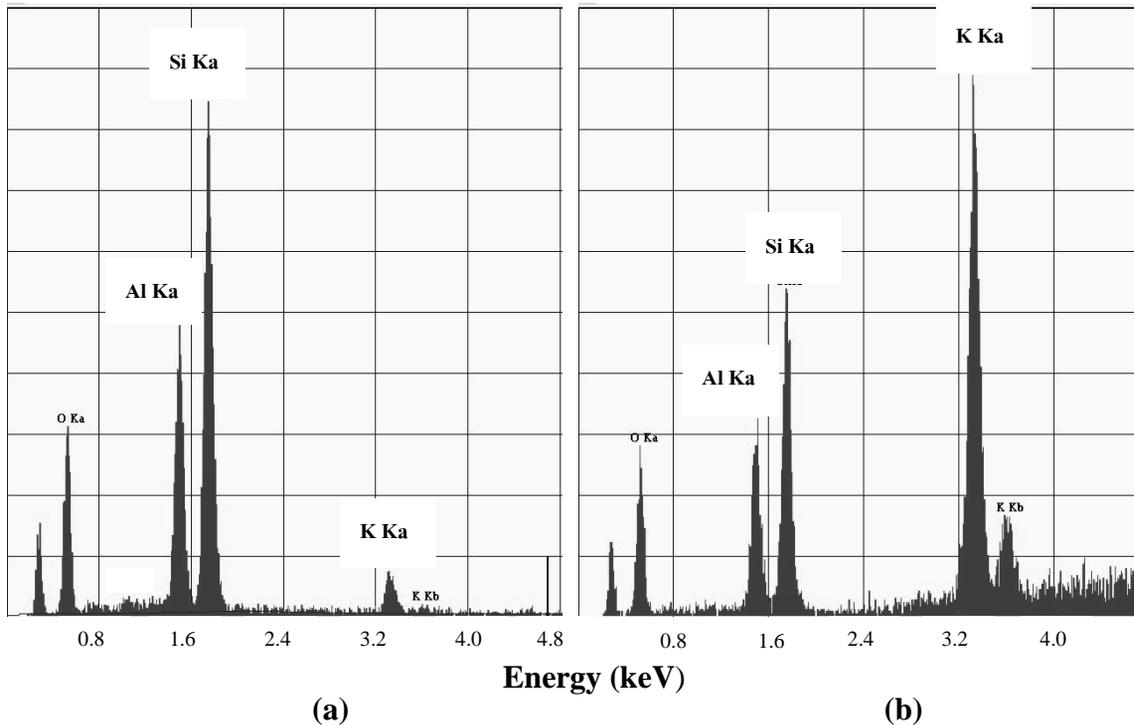
of volatile materials such as manganese oxide and iron ochre<sup>22</sup>. Bubbles were formed from the released gases under the vitrified skin due to pyroplastic nature of the vitrified body. When the ware was fired too rapidly, the volatile gases produced from organic matters or other sources could not escape because the surface layer had become vitreous. However, such volatile compounds did not seem to be responsible for the defects in the TC clay samples since the thermal analysis results confirmed that all the decomposition reactions had already completed before vitrification took place.

EDX point analysis on a non-defect area in comparison with a defect area (Fig. 4(a) and (b)) indicated that the defect area had an extremely high potassium content. It was believed that these areas were possibly filled with large particles of microcline. Bloating found in the TC clay samples was most likely due to the rapid melting of the over-fired microcline particles. Since it was vitreous but rather plastic at high temperature, the air bubbles occurred during melting of microcline were trapped within the melted volume. The trapped gas expanded upon heating, causing eruptions through the surface.

To clarify the cause of bloating and also poorer mechanical strength, TC clay was ball-milled for 5 hours in deionised water in order to reduce the size of the microcline particles. After milling, the clay powder was dried and uniaxially pressed at 50 MPa to form disc

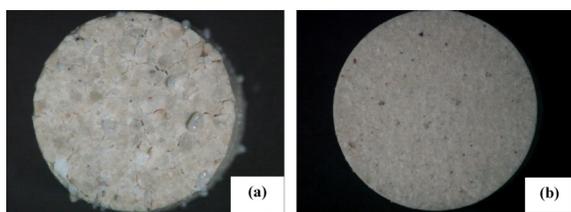


**Fig 3.** (a) OM image of the bloating area showing bubbles inside. (b) Cross-sectional SEM micrograph showing the origin of the bloating.



**Fig 4.** EDX point analysis on the (a) non-defect and (b) defect areas.

samples and fired at 1250 °C. Bar samples for mechanical testing were prepared by the previously described method. The comparative OM pictures of the TC clay sample prepared with and without ball milling showed that the surface defects which could obviously be seen in Fig. 5(a) disappeared when the TC clay powder was ball-milled (Fig. 5(b)). Besides, the bending strength result also showed that the milled TC clay had an average bending strength value of  $329 \pm 67$  kg.cm<sup>-2</sup>, which was almost two-fold of the value obtained from the sample prepared without ball-milling. The improved bending strength of this clay was thus attributed to the disappearance of the bubble defects or bloating by the ball milling process.



**Fig 5.** TC clay prepared (a) without ball milling and (b) with ball milling.

## CONCLUSION

TC clay contained high quantity of potassium-rich minerals, namely microcline and muscovite. It contained lower quartz content and thus higher clay-to quartz ratio than RC clay. Upon drying and firing, TC clay had higher shrinkage but lower water absorption compared with RC clay. TC clay started to deform significantly after firing at 1250 °C, possibly due to the high flux content in this clay that made it less resistant to warping than RC clay. RC clay, in contrast, contained higher quartz but lower microcline content than TC clay. Since it had relatively high quartz content, drying and firing shrinkage of RC clay sample was relatively low while its refractoriness was rather high. RC clay exhibited higher bending strength than TC clay after firing at 1250 °C, although it was not yet vitreous at this firing temperature. The poor mechanical strength of TC clay was proved to be due to bloating, which was caused by the large microcline particles in its body. The great improvement of the mechanical strength was achieved when TC clay was ball milled to reduce the size of the microcline.

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