Examination of ball clays derived from a new seam in northern Thailand

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Abstract. Domestic ceramic industrial demand requires intensive searches for a new source of ball clay with acceptable quality. Analysis of clay samples derived from a new seam in Payao province, northern Thailand was performed using a series of techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), laser diffraction, thermogravimetric analysis (TGA) and L*a*b* color space method. Geological study of this clay seam showed the division into 5 sub-layers, from top to bottom, and was coded as K₉, K₈, K₇, K₆ and K₅ respectively. The main minerals found in these clays were illite, quartz, kaolinite and rutile with a trace of clinochlore. K₅ was quartzitic with a relatively low clay mineral content. K₉ was reddish due to the high content of iron bearing mineral. This clay was least refractory so it was not attractive for high firing white ware industry. In K₆ layer, large particles of plant relicts were generally observed so it showed abnormal distribution of the particle size and a substantial thermal weight loss. K₇ and K₈ showed the greatest potential for utilisation in whiteware industry. These clay samples were off-white after firing at 1150 °C.

1. Introduction
Clay minerals are essential components of soil and sedimentary rocks. Types and contents of the constitute minerals found in the soil were reported to affect the properties because they possess unique structure and surface properties [1-3]. Ball clay is a group of sedimentary kaolin which mainly contains kaolinite as the main clay mineral and possibly quartz, mica and feldspar. Kaolinite is a dioctahedral 1:1 layer sheet structured hydrated aluminosilicate, whose theoretical formula is Al₂Si₂O₅(OH)₄, formed by superposition of silicon tetrahedral sheets and aluminum octahedral sheets via sharing of apical oxygen atoms [4,5]. Ball clay is prominent for its high plasticity which is a property of clay-water system [6].

In additions, ball clay contains some carbonaceous compounds, together with fine grained size, resulting in high plasticity and excellent drying strength. Generally, ball clay exhibits high drying and firing shrinkage which sometimes can cause internal cracking and thus poor mechanical properties. A wide variation of compositions and particle size ranges results in different characteristics for individual clay seams within a deposit. The particle size or size distribution of clay minerals is a key parameter for mineral identification. It has been recommended that separation and extraction of clay
fractions (i.e., <2 μm particles) is performed for qualitative and quantitative analysis, at least for clay minerals.

In ceramic industry, ball clay is widely mixed with china clay to produce a workable and malleable clay body [4]. Colours in ball clay may be varied in a wide range from grey, yellow, red, brown and black depending on level and types of colouring impurities. Some ball clay may contain illite (K<sub>4</sub>Al<sub>4</sub>Si<sub>8-y</sub>Al<sub>y</sub>O<sub>20</sub>(OH)<sub>4</sub>) which is classified as a clay mineral mica, mica or other fluxing minerals [7,8]. The fine particle sized illite was useful for low firing scheme. Measuring of particle size distribution would help in estimation of the permeability of a clayey material, which constituted an important property for ceramic paste during shaping process [9].

Ball clay has found many industrial applications especially in traditional ceramic industry. It is also used extensively to increase plasticity in some modern ceramic bodies such as cordierite-mullite refractory [10]. Thai traditional ceramic industry has played an important role in promotion of Thai economics. The annual export value of Thai traditional ceramics was about 1 billion dollars annually and ball clay is one of the main ingredients used in these products. Industrial ceramic firing process also requires the use of cordierite-mullite kiln furniture which partly contains imported ball clay. The white firing ball clay with fine grain size of less than 0.5-1 μm, in general, is valued for ceramic industry [11].

While domestic industrial demand is still high, the source clay with acceptable quality becomes scarce. There is a need to look for a new source of ball clay supply which can serve industrial scale demand. Recently a new ball clay seam has been discovered in Payao province, northern Thailand. Characterisation of the clay for the purpose of future industrial use was addressed in this paper.

2. Experiments

The clay seam is located at 19° 11’ 30″ N, 99° 52’ 42″ E, Thailand. Geological studies done by a private company using a wash boring process with a rotary hydraulic feed showed that this seam could be divided horizontally into 3 layers. The top-most layer clay was coded as K<sub>R</sub>. This clay, reddish, brownish or greyish in color, is silty sand. The depth of this layer was less than 2.0 m. The next layer underneath K<sub>R</sub> was clayey with the colour ranging from dark grey to black and can be divided into 3 sub-layers, from top bottom, namely K<sub>C</sub>, K<sub>A</sub>, and K<sub>B</sub> respectively. This layer was around 3.0-4.5 m thick, and found at around 1.2 to 1.6 m depth from the top surface. The bottom-most layer was silty to coarse sand with brownish pink to yellowish pink in colour. This layer had a thickness around 0.5-3.5 m and was coded as K<sub>Q</sub>.

Samples of clays from each layer were crushed and sieved through a 25-mesh stainless steel sieve, then dried in an oven pre-set at 110°C for 24 hours prior to characterisation. Chemical analysis was performed using an XRF (Horiba, Japan). Particle size distribution (PSD) of the milled mud was measured using a particle size analyzer (Malvern Instruments Limited, UK). Phase and microstructure analysis were performed using an X-ray diffraction (XRD) technique equipped with the software X’pert High Score Plus (X’pert Pro MPD, Philips, Netherlands) and scanning electron microscope (SEM: LEO 1450 VP). Thermal decomposition of the clay powders was examined using a TGA/SDTA 851° STAR<sup>®</sup> thermobalance (Mettler Toledo, Switzerland). Fired colours (at 1150 °C/1 h.) were measured using the L*a*b* color space method (Hunter Lab, ColorFlex EZ Spectrophotometer).

3. Results and Discussions

Chemical analysis of the clay samples from each pit (Ø ~7.5-10.0 cm) is presented in Table 1. Chemical composition of the raw clay samples was one of the significant indicators used for clay selection in ceramic products [11]. Commonly Al<sub>2</sub>O<sub>3</sub>, with a pronounce effect on refractoriness and mechanical strength of the final product, was the prime constituent to look at. Too high content of SiO<sub>2</sub> could deteriorate plasticity and refractoriness. Colouring oxides such as titanium and iron could not only damage the whiteness but also give a fluxing action. The presence of calcium oxide could also give a negative effect in degradation of structural-mechanical properties, decreased fluidity and
liquescence of the slip [12]. Only $K_A$, $K_B$ and $K_C$ showed an amount of $Al_2O_3$ of greater than 20%. The $Al_2O_3$ was, however, relatively low in the $K_Q$, suggesting the low content of clay minerals. While the amount of $TiO_2$ was in the same range in all clays, $Fe_2O_3$ was extremely high in $K_R$ and progressively lower in the lower layers. $SiO_2$ content was highest in $K_Q$ and lowest in $K_B$. Variation of the fluxing oxides such as $CaO$ or $K_2O$ was not in a great degree.

Table 1. Chemical analysis of clays from various layers.

| Oxides    | $K_A$  | $K_B$  | $K_C$  | $K_R$  | $K_Q$  |
|-----------|--------|--------|--------|--------|--------|
| $SiO_2$   | 73.800 | 69.235 | 72.327 | 71.735 | 80.859 |
| $TiO_2$   | 1.077  | 1.304  | 1.140  | 0.960  | 0.809  |
| $Al_2O_3$ | 20.243 | 23.938 | 21.245 | 17.198 | 14.628 |
| $Fe_2O_3$ | 1.937  | 2.707  | 2.084  | 6.767  | 0.920  |
| $CaO$     | 0.106  | 0.224  | 0.111  | -      | -      |
| $MgO$     | -      | -      | 0.871  | 0.896  |        |
| $K_2O$    | 2.836  | 2.592  | 3.094  | 2.463  | 1.845  |
| $ZrO_2$   | -      | -      | -      | -      | 0.041  |

Phase analysis results based on XRD of the raw clays received from the same pit are graphically shown in Fig. 1.

Figure. 1. XRD spectra for sample clays received from various layer of the same pit. (I: illite, Q: quartz, K: kaolinite, R: rutile, L: Lepidocrocite).
The main minerals found in these clays were illite, quartz, kaolinite and rutile. Traces of reflections according to Clinohlore or iron magnesium aluminium silicate hydroxide ((Mg, Al)$_6$ (Si, Al)$_4$O$_{10}$(OH)$_8$), Reference code: 00-012-0242), could be observed at the positions $\sim 12.5$ and $18.8^\circ$. The results showed that $K_C$ and $K_A$ are kaolinitic while $K_Q$ was quartzitic with only a small amount of kaolinite detected. It was also noted that $K_B$, which was located adjacent to $K_Q$, showed only a small quantity of kaolinite mineral. In $K_R$, extra reflections belonging to Lepiodocrocite (FeO(OH), Reference Code: 01-074-1877) appeared at the position $\sim 14.15^\circ$. The presence of this mineral was thus believed to be responsible for the reddish colour of this clay.

Particle size distribution (PSD) analysis of the clays from each layer is shown in Figure 2. Geologically clay is defined as a naturally occurring material composed primarily with finely grain minerals of particle size less than 2 $\mu$m [13]. Agglomeration of the clay particles could, however, be suggested from this experiment as most clay powder showed the size of greater than 2 $\mu$m. $K_A$ and $K_C$ have a very similar symmetrical distribution curves of particle size with the smallest average size of all. $K_B$, however, showed an asymmetrical distribution as a broad peak suggesting a wide variation of powder size and shapes. $K_R$ showed the highest number of fine particles of size less than 1 $\mu$m. These particles agglomerated into larger particles with an average size of $\sim 6-7 \mu$m. The shift to the larger size of the same size range was also found in $K_Q$.

![Figure 2](image_url) **Figure 2.** Particle size distribution of the sieved clay powders. (--- $K_A$, $K_B$, $K_C$, $K_R$, $K_Q$).

SEM micrographs in Fig. 3 revealed platy shaped particles of clay minerals in all clay powders with largest plate size and more perfect plates observed in $K_A$. It was noted that in $K_B$ there were coexistence of large plant relict particles with the clay particles (Fig. 3c). $K_R$ showed the highest amount of fine fractured particles which was in good agreement with the PSD analysis.
Figure 3. SEM micrographs showing platy particles for different clays sieved through a 25-mesh sieve (a) $K_A$, (b) $K_B$, (c) $K_B$ - showing a plant relict, (d) $K_C$, (e) $K_R$ and (f) $K_Q$.

Thermograms of the clay powders measured in the temperature range between room temperature to 1000 °C are shown in Figure 4. The result revealed that $K_B$ contained a substantial amount of decomposable matters due to the plant relict coexistent with the clay particles. $K_Q$ which mainly contained quartz mineral had only $\leq 2\%$ of weight loss. $K_R$, $K_A$, and $K_C$ exhibited the weight loss of around 5-10%. This result suggested that the use of $K_B$ in ceramic industry may not be suitable due to this super high weight loss. $K_Q$ which mainly contained quartz mineral could also introduce problems with its lack of plasticity and refractoriness as the amount of clay mineral was too small.

Figure 4. Thermogravimetric analysis of the clay powders obtained from different layers.
The colour measurement in L* a* b* units are shown in Table 2. L* is the luminance or lightness component, which ranges from 0 to 100, and parameters, a* (from green to red) and b*(from blue to yellow) are the two chromatic components, which range from -120 to 120 (León 2006). The colour measurement was not achieved in the fired compacted K\textsubscript{R} as it could not be fired to such temperature. The low temperature firing of red clay was unsurprised as the clay particles were finer and as it accommodated a great amount of fluxing minerals, both in the structure and as free minerals. This result suggested that the fired colour of these clays was off-white so utilisation for white wares may be at a limited content.

| Unit | K\textsubscript{A} | K\textsubscript{B} | K\textsubscript{C} | K\textsubscript{Q} |
|------|----------------|----------------|----------------|----------------|
| L*   | 77.5           | 77.6           | 74.6           | 80.8           |
| a*   | 7.7            | 8.4            | 9.5            | 5.3            |
| b*   | 20.5           | 20.6           | 23.4           | 13.8           |

4. Conclusion

Full analysis of the clays derived from different layers in this new seam suggested that K\textsubscript{A} and K\textsubscript{C} showed the greatest potential for utilisation in white ware industry. Further examination of this clay for different forming approaches such as slip casting or plastic foaming will be useful. K\textsubscript{B} which showed a substantial weight loss upon firing due to the presence of organic matters was not suitable to use in products which involves heating. K\textsubscript{R} which contained the greatest amount of fine clayey matters with reddish colour according to the iron-bearing minerals would not be suitable for refractory products. K\textsubscript{Q} was rather quarsitic so it was not suitable to be used for the products that required forming plasticity.

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