EFFECT OF FIRING CONDITIONS ON PROPERTIES OF DAN KWIAN POTTERY

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Abstract

Dan Kwian pottery is a unique and legendary pottery which brings a large amount of revenue to Nakhon Ratchasima province. However, most of the factories in Dan Kwian are still using basic production techniques which have been used for many decades. This is especially true of the firing technique. At present, most factories in Dan Kwian are firing their greenware in traditional wood-burning kilns. They have low efficiency and the temperatures inside are not uniformly distributed. The influence of the firing conditions on the properties of Dan Kwian pottery was studied in this work in order to obtain data for improving kiln efficiency. Test samples prepared from Dan Kwian clay were fired under different conditions in electric and Dan Kwian kilns. Then, their color and physical properties were tested, calculated, and compared. Data were statistically analyzed using ANOVA. Results showed that samples fired at 900°C and 1200°C under an oxidizing atmosphere have comparable properties to samples fired in Dan Kwian kilns by the red (at 1085°C) and black (at 1250°C) firing methods, respectively. These findings suggest that, if the temperature inside Dan Kwian kilns can be made more homogeneous, then the Dan Kwian firing temperature can be reduced.

Keywords: Dan Kwian, pottery, ceramic, firing

Introduction

Dan Kwian is a ceramic producing village located in Dan Kwian subdistrict, Chok Chai district, Nakhon Ratchasima province, Thailand. Dan Kwian is well known forits unique pottery and handicraft products which are widely used for interior and outdoor decoration. Factories at Dan Kwian use the clay from the banks of the Moon River to produce their pottery. The uniqueness of Dan Kwian pottery comes from the Dan Kwian clay which has small particle sizes and high-plasticity; therefore, it can be easily formed into beautiful pottery shapes. Moreover, the most special characteristics of Dan Kwian

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clay are that, after firing, it has high durability and toughness. It has a rusty red color that is believed to come from iron oxide in the clay. Dan Kwian pottery brings both reputation and large amounts of income to Nakhon Ratchasima province (Chimnakom, 1999). However, most of the factories in Dan Kwian district are still using basic production techniques that have been used for many decades. This is especially true of the firing technique. Pottery in Dan Kwian was traditionally fired in 2 distinctive styles which are known asblack fired and red fired. Black fired potteryis fired to temperatures of approximately 1200-1250°C (Chimnakom, 1999). Pottery fired in this style is dark brown, vitreous, and has high durability and low porosity. This firing style is primarily used for producing Dan Kwian water jars and mortars. Dan Kwian red fired style pottery is fired to temperatures of approximately 900-1100°C. Pottery made in this firing style is used for earthen ware pots, tiles, interior and outdoor decorations, and handicrafts. It has a rusty red color and high porosity.

Kilns are an essential part of Dan Kwian factories since they are requiredto fire the pottery. The Dan Kwian kiln is a wood burning kiln of similar design to the Anagama kiln (Wikipedia Foundation, Inc., 2013). Figures 1 and 2 show a Dan Kwian kiln. Although wood is not difficult to find, its price continuously increases. Moreover, smoke released from burning wood pollutes the air and disturbs people in the nearby community. The purpose of this work was to study the effect of the firing conditions on the properties of Dan Kwian pottery. The information from this study is beneficial for improving the firing of Dan Kwian pottery byreducing energy consumption and air pollution in Dan Kwian village.

Materials and Methods

In this work, mixed and kneaded Dan Kwian pottery clay that was ready to be made into pottery was collected from a factory in Dan Kwian village. The clay was analyzed by X-ray fluorescence (XRF) and divided into 2 portions. The first portion was used to study the thermal properties of unfired Dan Kwian pottery clay. The second portion was used to studythe physical properties of the pottery clay after firing. The reflectance spectra were studied for the fired pottery clay. To determine the thermal properties, a Perkin Elmer Model DTA7 differential thermal analyzer (Perkin Elmer, Inc., Waltham, MA, USA) and a Netzsch dilatometer Model 402 EP (Netzsch-Gerätebau GmbH, Selb, Germany) were employed for differential thermal and dilatometric analysis of unfired Dan Kwian pottery clay, respectively. Dan Kwian pottery clay was extruded and cut into 500 specimen bars of dimensions 10×20×100 mm. The specimen bars were dried at 100°C before

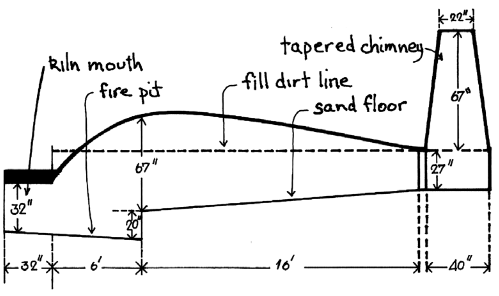

Figure 1. Side view of Dan Kwian kiln (Chimnakom, 1999)

Figure 2. A kiln operator loading wood into a Dan Kwian kiln

being fired at the 10 firing conditions as shown in Table 1. The first tothe fourth firing conditions (OX500, OX700, OX900, and OX1200) were in an oxidized atmosphere. Specimen bars were put into open saggars and fired to the preset temperatures of 500, 700, 900, or 1200°C in an electric kiln with a heating rate of 5°C/min and a 1 h soaking time. Afterwards, they were cooled to room temperature at a rate of 5°C/min. The fifth and the sixth firing conditions were in Dan Kwian kilns at a Dan Kwian factory in the typical Dan Kwian red and Dan Kwian black (DKrd and DKbk) firing conditions. Figure 3 depicts the temperature profiles of DKrd, DKbk, OX700, and OX1200). It can be seen that the maximum temperatures for the DKrd and DKbk firing conditions are 1085 and 1250°C, respectively. The seventh to the tenth firing conditions (RD500, RD700, RD900, and RD1200) were in a reduced atmosphere. Samples were buried under rice husk charcoal in closed saggars and fired in an electric kiln to the temperatures of 500, 700, 900, and 1200°C with the same temperature profiles as in the first to the fourth firing conditions. Then the postfiring properties of the Dan Kwian clay were determined following the ASTM: C1161-02C (ASTM International, 2002) and ASTM: C373-88 (ASTM International, 1994) methods. Approximately 30 samples were tested for each firing condition. Design Expert® software (Stat-Ease, Inc., Minneapolis, MN, USA) was used to doanalysis of variance (ANOVA). The 350-700 nm reflectance spectra of the fired samples were measured by using a Hunter Lab Model Ultra Scan XE spectrophotometer (Hunter Associates Laboratory, Inc., Reston, VA, USA). Approximately 30 samples were tested for each firing condition in Table 1.

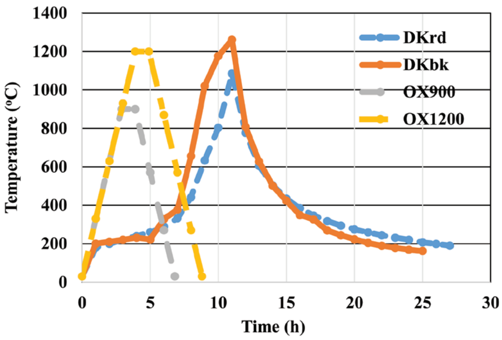

Figure 3. Temperature profiles of the DKrd and DKbk firing conditions recorded from a Dan Kwian pottery factory compared to the OX700 and OX1200 firing conditions. Note that the maximum firing temperatures of the DKrd and DKbk firing conditions were 1085°C and 1251°C, respectively

Table 1. Firing conditions for firing Dan Kwian clay

	Firing condition	Maximum temp (°C)	Abbreviation
1	Oxidation	500°C	OX500
2	Oxidation	700°C	OX700
3	Oxidation	900°C	OX900
4	Oxidation	1200°C	OX1200
5	Dan Kwian red	~1085°C	DKrd
6	Dan Kwian black	~1260°C	DKbk
7	Reduction	500°C	RD500
8	Reduction	700°C	RD700
9	Reduction	900°C	RD900
10	Reduction	1200°C	RD1200

Results and Discussion

Chemical and Thermal Analysis Studies

A) Chemical analysis

The major chemical compositions of Dan Kwian pottery clays obtained from XRF analysis are 75% SiO_2, 16% Al_2O_3, 5% Fe_2O_3, and 1% K_2O.

B) Differential thermal analysis (DTA)

This analysis measuresthe temperature change of samples during heating. The measurement provides information about chemical reactions, phase transformations, and structural changes that occur in a sample during heating and cooling. Figure 4 is a DTA plot for unfired Dan Kwian pottery clay. There are 4 peaks in this DTA result. These peaks are explained by Grim and Rowland (1942) as following:-

a) An endothermic peak at about 100°C due to the removal of hygroscopic water;
b) An exothermic peak between 250-500°C due to the organic burnout;
c) An endothermic peak at 573°C due to quartz transformation; and
d) An exothermic reaction peak at about 950°C that is probably due to oxide recrystallization.

C) Dilatometer analysis

This analysis measures the dimensional change of material during heating. This measurement not only provides the thermal expansion coefficient of a sample, but it also gives information about phase and crystalline transformationsas well as shrinkages. Figure 5 is a dilatometricplot of unfired Dan Kwian clay. It is clear that Dan Kwian clay slightly expands when heated from room temperature to 100°C. After that it shrinks during heating between 100-200°C. This is probably due to the loss of hygroscopic water. When heated from 200 to 570°C, Dan Kwain clay expands slowly. However, between 570 to 580°C it expands greatly because at 573°C there is the quartz transformation temperature. Upon further heating from 580-860°C, Dan Kwian clay slowly shrinks due to the collapse of the clay structure from the dehydroxilation process and it startsto form vitreous phases (McKinstry, 1965). Finally, Dan Kwian clay shrinks much faster when heatedat a temperature higher than 860°C because of the vitreous phase and recrystallization process as was observed in the DTA study (Grim and Rowland, 1942).

Physical Properties of Fired Pottery Clays

The following properties of Dan Kwian clay fired under different conditions were determined:

a) Linear firing shrinkage
b) Weight loss
c) Modulus of rupture
d) Apparent porosity
e) Water absorption

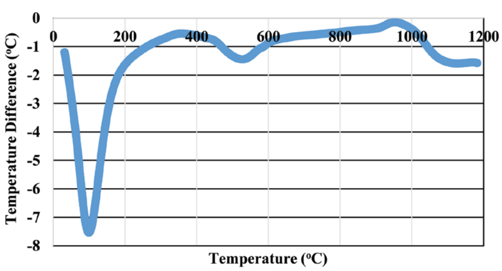

Figure 4. The DTA curve of Dan Kwian pottery clay tested with a 20°C/min heating rate

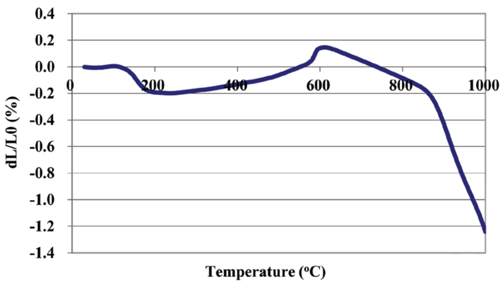

Figure 5. The dilatometer plot of Dan Kwian clay

f) Apparent specific gravity
g) Bulk density

a) Linear firing shrinkage is the change insample size caused by firing. The dry length (L_d) and fired length (L_f) of 30 specimens of each firing condition were measured. Linear firing shrinkages were calculated from the following equation:

$$Linear\ \ firing\ shrinkage\ (\%) = \frac{(L_d \times L_f)}{L_d} \times 100 \qquad (1)$$

Table 2 and Figure 6 show the linear firing shrinkage of Dan Kwian clay fired under different conditions. It is clear that the linear firing shrinkages of Dan Kwian clay are less than 1% when fired under all firing conditions except at OX1200, DKbk, and RD1200.

Data were analyzed using ANOVA. The results in Table 3 indicated that the firing condition significantly affects the linear firing shrinkage of Dan Kwian clay. This is because the p-value of the firing condition is less than 0.05 (Anderson and Whitcomb, 2005). To comparethe linear firing shrinkage of each firing condition to others, statistical software was employed to perform t-tests on all pairs of mean linear firing shrinkage values under all firing conditions. The results showed that the Prob > |t| of the differences in the mean linear firing shrinkage within the groups below was greater than 0.1:

1) OX500 = RD700
2) OX900 = DKrd = RD500 = RD900
3) OX1200 = DKbk

The results indicated that Dan Kwian clay within the groups above statistically has the same firing shrinkage (Anderson and Whitcomb, 2005).

b) Weight loss is the percentage weight loss of the dry sample after being fired. Weight loss can be calculated using the following equation:

$$Weight\ loss\ (\%) = \frac{(W_d - W_f)}{W_d} \times 100 \qquad (2)$$

Table 2. Average values of properties of Dan Kwian pottery clay fired at different firing conditions

	OX500	OX700	OX900	OX1200	DKrd	DKbk	RD500	RD700	RD900	RD1200
Linear firing shrinkage (%)	0.28	0.07	0.15	3.42	0.16	3.43	0.14	0.28	0.17	1.36
Weight loss (%)	1.39	4.65	5.50	6.06	4.66	6.12	1.32	3.06	5.64	6.46
Modulus of Rupture (MPa)	3.18	2.21	5.86	8.98	3.10	9.06	2.71	4.29	4.99	11.76
Apparent porosity (%)	32.58	29.79	30.63	20.90	30.37	20.73	-*	29.02	29.66	26.80
Water absorption (%)	17.65	15.90	16.29	10.31	16.20	10.19	-*	15.06	15.90	15.60
Apparent specific gravity (unitless)	2.73	2.67	2.69	2.57	2.69	2.57	-*	2.72	2.65	2.35
Bulk density (g/cm^3)	1.84	1.87	1.87	2.03	1.87	2.04	-*	1.97	1.87	1.72

* *There is no data on the properties after firing of Dan Kwian clay fired under the RD500 condition because the samples decomposed into powder during boiling, according to the ASTM testing procedure.*

where W_d and W_f are the dry and fired weight, respectively. Table 2 and Figure 7 show the weight loss of Dan Kwian clay fired under different conditions. It is clear that the higher firing temperatures resulted in larger weight losses. Statistical analysis shows that the firing condition has a significant effect on weight loss. The differences in weight loss among the pairs below were statistically insignificant:

1) OX500 = RD500
2) OX700 = DKrd
3) OX1200 = DKbk

c) The modulus of rupture or flexural strength is the ultimate strength of a beam in bending. The standard formula for the strength of a beam in a 3-point flexural test is:

$$Modulus\ of\ Rupture\ (MOR) = \frac{3P_f l}{2bd^2} \qquad (3)$$

where P_f is the breaking force in Newtons, b and d are the width and thickness of the specimen in meters, respectively, and l is the outer support span in meters. Table 2 and Figure 8 give the average modulus of rupture of Dan Kwian clay fired under different conditions. It can be seen that most data show that the higher firing temperatures result in a higher MOR. Statistical analysis shows that the firing condition has an important effect on the modulus of rupture. Differences in the modulus of rupture within the sample groups below were statistically insignificant:

1) OX500 = DKrd
2) OX900 = RD900
3) OX1200 = DKbk

d) Apparent porosity is the relationship of the volume of aspecimen's open pores to its

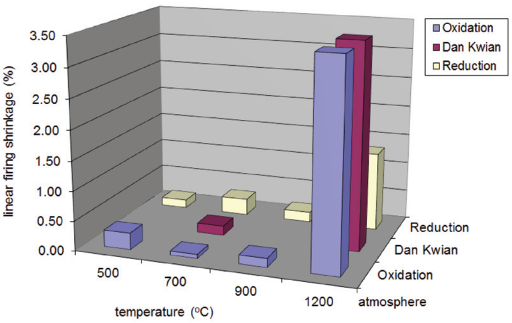

Figure 6. Average linearfiring shrinkages of Dan Kwian pottery clays fired under different conditions

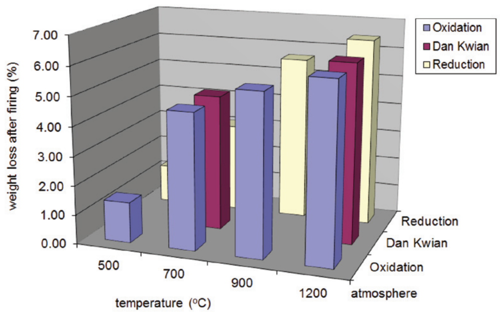

Figure 7. Average weight losses of Dan Kwian pottery clays fired under different conditions

Table 3. The Analysis of variance table (ANOVA) table of linear firing shrinkage of Dan Kwian clay after being fired in different firing conditions

Source	Sum of Squares	df	Mean Square	F-Value	p-value
Model	76.75	9	8.53	665.26	< 0.0001
Firing conditions	*76.75*	*9*	*8.53*	*665.26*	*< 0.0001*
Pure Error	5.99	467	0.013		
Cor Total	82.74	467			

* *ANOVA results of weight loss, modulus of rupture, apparent porosity, water absorption, apparent specific gravity, and bulk density are similar to Table 3; therefore, they are not shown.*

exterior volume. It can be calculated from the following equation:

$$Apparent\ porosity\ (\%) = \frac{(M-D)\,x\,100}{(M-S)} \quad (4)$$

where M, D, and S are the saturated, dry, and suspended in water weights, respectively. Figure 9 and Table 2 show the average apparent porosity of Dan Kwian clay fired under different conditions. For Dan Kwian clay fired at the same temperature, the apparent porosity of the clay fired under oxidizing conditions was higher than under reducing conditions. This is because more organic material can be burned out of the clay under oxidizing conditions than under reducing conditions. The burned out organic material leaves the pores in samples. The t-tests on the average apparent porosity of all pairs indicated that the differences among the following pairs were statistically insignificant:

1) OX700 = RD900
2) OX900 = DKrd
3) OX1200 = DKbk

e) Water absorption is the ratio of the mass of water absorbed to the mass of the dry specimen. It can be calculated as follows:

$$Water\ absorption\ (\%) = \frac{(M-D)\,x\,100}{D} \quad (5)$$

where M and D arethe specimen dry and saturated weights, respectively. Table 2 and Figure 10 illustrate the water absorption of Dan Kwian clay fired under different conditions. It can be seen that the water absorption of the OX1200 and DKbk fired samples was much lower than that of other firing conditions. This is probably because Dan Kwian clays fired under the OX1200 and DKbk conditions shrink considerably compared to other firing conditions. This result corresponds well to the linear firing shrinkage and dilatometer results in previous sections. Statistical analysis indicates that differences in water absorption within the following pairs offiring conditions were insignificant:

1) OX700 = RD900
2) OX900 = DKrd
3) OX1200 = DKbk

f) Apparent specific gravity is the ratio of a mass of solid to the mass of an equal volume of water andcan be calculated as follows:

$$Apparent\ specific\ gravity = \frac{D}{(D-S)} \quad (6)$$

where D and S are the specimen dry and suspended in water weights, respectively. The apparent specific gravities of Dan Kwian clays fired under different conditions are shown in Figure 11 and Table 2. Most data show that Dan Kwian clays fired to higher temperatures have lower apparent specific gravities than those are fired to lower temperatures. The t-tests on all pairs of

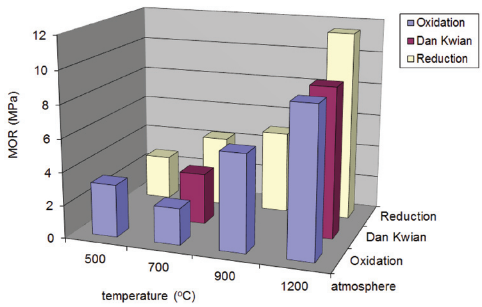

Figure 8. Average modulus of ruptures of Dan Kwian pottery clays fired under different conditions

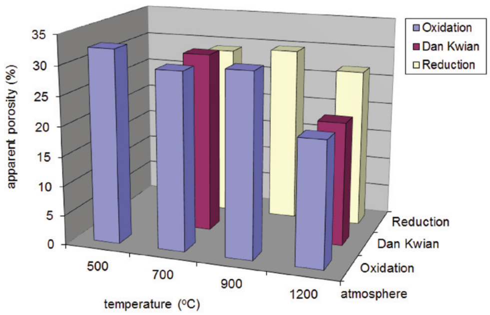

Figure 9. Average apparent porosities of Dan Kwian pottery clays fired under different conditions

average apparent specific gravity values indicated that the apparent specific gravity of the samplepairs belowwere not statistically significant.

1) OX900 = DKrd
2) OX1200 = DKbk

g) Bulk density is the ratio of specimen dry mass divided by it exterior volume including pore volume. It is calculated using the following equation:

$$Bulk\ density\ (g/cm^3) = \frac{D}{(M - S)} \qquad (7)$$

where D, M, and S are the specimen dry, saturated, and suspended in water weights, respectively. Figure 12 and Table 2 present the average bulk densities of Dan Kwian clays fired under different conditions. It is clear that when the firing temperature is increased, Dan Kwian clay fired under an oxidizing atmosphere has a higher bulk density. This is, however, not the case for Dan Kwian clay fired under reducing conditions. Statistical analysis shows that the following samples have the same bulk density within the groups below:

1) OX700 = OX900 = DKrd = RD900
2) OX1200 = DKbk

Reflectance Spectra

Figure 13 illustrates the reflectance spectra of Dan Kwian clay fired under an oxidizing atmosphere. The reflectance spectra between 570-700 nm increase as thefiring temperature is increased from 500 to 900°C. This wavelength covers the visible range of color from yellow to red. The result indicates that, under oxidation conditions, fired Dan Kwian clays develop more yellowish and reddish hues as the firing temperature is

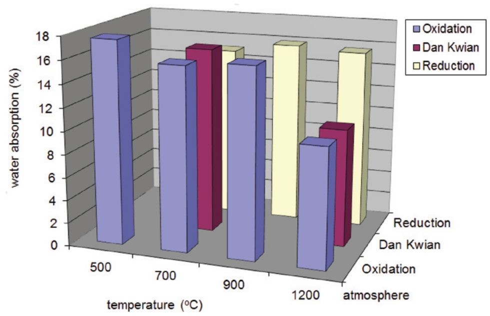

Figure 10. Average water absorption of Dan Kwian pottery clays fired under different conditions

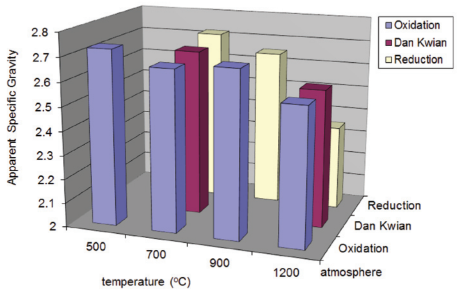

Figure 11. Average apparent specific gravities of Dan Kwian pottery clays fired under different firingconditions

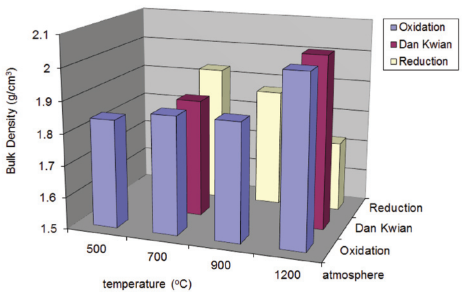

Figure 12. Average bulk densities of Dan Kwian pottery clays fired under different firing conditions

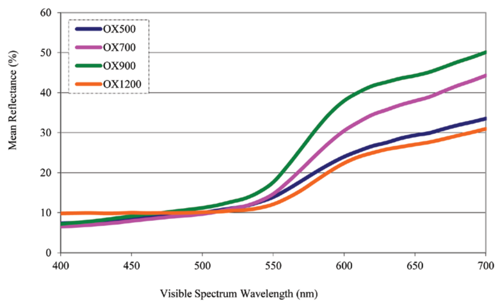

Figure 13. Reflectance spectra of Dan Kwian clays fired under oxidation atmosphere

increased from 500 to 900°C. The reflectance spectra between 400-500 nm increase and between 500-700 nm decrease as the firing temperature is increased from 900 to 1200°C. This result suggests that Dan Kwian clay will have a darker color as it is fired to higher temperatures from 900 to 1200°C since the 400-500 nm wavelength range has violet, indigo, and blue colors and the 500-700 nm wavelength range has green, yellow, and red colors. The reflectance spectra of Dan Kwian clay fired in a reducing atmosphere is not measured, because during firing under these conditions charcoal covered and attached to the samples. Figure 14 shows the reflectance spectra of samples fired in DKrd, OX700, and OX1200 conditions. The spectral plot of the sample fired in the DKrd firing condition is almost the same as the sample fired in the OX700 condition. There is no OX firing condition which has the same reflectance spectra as the DKbk firing condition. The OX firing condition which has the closest reflectance spectra to DKbk is OX1200, as shown in Figure 14. Figure 15 illustrates the colors of ground Dan Kwian clays fired under different firing conditions. It confirms that the colors of Dan Kwian clay fired under OX1200 and DKbk are almost the same as are the colors under the OX700 and DKrd firing conditions. In addition, the colors of Dan Kwian clay fired under OX900 and DKrd are almost identical.

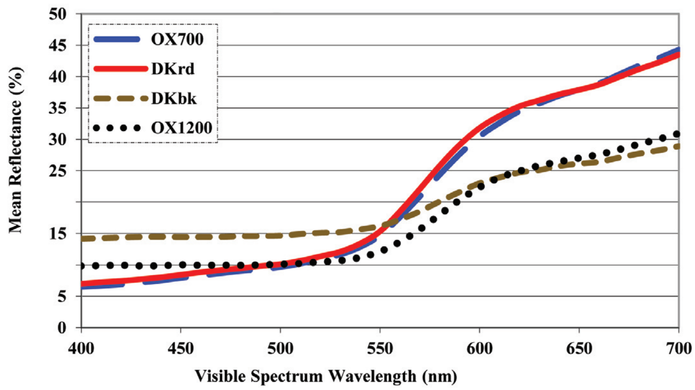

Figure 14. Reflectance spectra of Dan Kwian clays fired under DKrd, DKbk, OX700, and OX1200 firing conditions

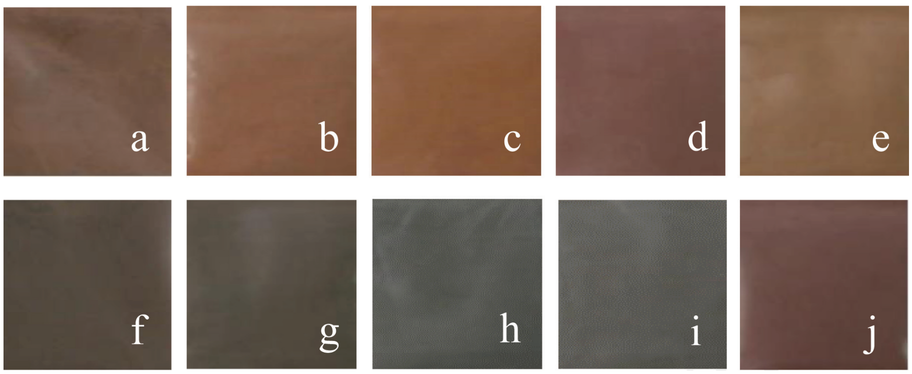

Figure 15. Ground Dan Kwian clay fired under different firing conditions: a) OX500, b) OX700, c) OX900, d) OX1200, e) DKrd, f) RD500, g) RD700, h) RD900, i) RD1200, and j) DKbk

Table 4. The firing conditions which give the same after firing properties as the DKrd and DKbk firing conditions

	DKrd	DKbk
Linear firing shrinkage	OX900 RD500 RD900	OX1200
Weight loss	OX700	OX1200
Modulus of rupture	OX500 OX700 RD500	OX1200
Apparent porosity	OX900	OX1200
Water absorption	OX900	OX1200
Apparent specific gravity	OX900	OX1200
Bulk density	OX700 OX900 RD900	OX1200
Color	OX700	OX1200

Conclusions

Table 4 shows the firing conditions having the same clay properties as those of the DKrd and DKbk firing conditions. It can be seen that Dan Kwian clay fired under the OX1200 firing condition statistically has the same properties as Dan Kwian clay fired under the DKbk firing condition. This suggests that it is possible to fire Dan Kwian pottery at 1200^{o}C and produce pottery with the same physical properties as those fired under the DKbk firing condition. Since the maximum firing temperature of the DKbk process is 1250^{o}C, it will save energy if Dan Kwian clay pottery is fired to 1200^{o}C rather than 1250^{o}C. It was found that the energy consumption for firing ceramic from room temperature to 1000^{o}C is equal to the energy consumption for firing it from 1000^{o}C to 1200^{o}C (Sirisoonthorn, 2010). Thus, reducing the firing temperature from 1250^{o}C to 1200^{o}C can save considerable energy. This, consequently, can decrease smoke from the wood burning kilns and the resulting air pollution in the Dan Kwian community. Unfortunately, there is no single firing condition for Dan Kwian clay that can produce material with all the same properties as the clay fired under the DKrd firing condition. From Table 4, it can be seen that all properties of Dan Kwian clay fired under the OX900 firing condition are statistically the same as the DKrd firing condition except for weight loss, MOR, and color. The OX900 fired Dan Kwian clay has a greater weight loss and MOR and a brighter color than the DKrd fired Dan Kwian clay. Generally, ceramics fired to attain higher weight loss and MOR are better than those designed to haveless weight loss and lower MOR.In addition, the brighter color of OX900 fired Dan Kwian clay should be an acceptable changefor Dan Kwian pottery as acrylic decorated products.Therefore, it is possible to conclude that Dan Kwian clay firedunder the OX900 firing condition has either the same or better properties than Dan Kwian clay fired under the DKrd firing condition. This suggests the possibility of decreasing the DKrd firing temperature by 185^{o}C, since the maximum temperature for the DKrd process is 1085^{o}C and the maximum firing temperature for an OX900 process is 900^{o}C. This temperature reduction will result in much lower energy consumption and less air pollution.

The most serious problem remaining is that Dan Kwian kilnsdo not have an even temperature distribution. The front is nearer to the fireplace and tends to have higher temperatures than the back, so the position of pieces within the kiln distinctly affects the pottery's properties. It is suggested that the temperature homogeneity distribution within Dan Kwian kilns be improved before reducing the firing temperature.

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