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Effect of Limestone Dust on the Properties of Thai Pottery Sintering at Low Temperature

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Abstract

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Limestone dust from a limestone crushing plant was used as an additive in pottery clay for this experiment. After the limestone dust was sieved through a 35 mesh stainless steel sieve, it was mixed with Angthong pottery clay at various contents. Samples with and without limestone dust were sintered at 600, 700, 900, and 1000°C. Because of limestone blowing for samples with limestone dust sintered at 900 and 1000°C, physical property measurement was performed only for samples sintered at 600 and 700°C. While sintering at low temperatures (600 and 700°C), physical properties of samples with limestone dust were improved. Water absorption and linear firing shrinkage were reduced when limestone dust content increased and flexural strength increased when limestone dust content increased. Furthermore, no black coring was found in samples with limestone dust.

Key words : limestone dust, Thai pottery, low temperature

Introduction

Thai pottery is a local industry spreading in several parts of Thailand. The main purpose of making pottery for Thai people in rural areas is to use products as cooking ware such as pots and stoves or garden ware like flower pots or even water containers when their makes are traditional techniques. One example is the often employed technique of mixing clay with homemade coarse grog (fired mixture of clay and rice husk).

In big cities of this country, high technology industries are growing and there are a lot of building activities. As the result of building, the usage of certain materials such as cement, limestone and sand is increasing. Limestone grinding mills produce those materials for the building activities while dust from the mill is also produced as industrial waste. The main composition of dust is calcium carbonate. According to some researches, limestone or calcium carbonate could be used as a tempering agent. In the past, using limestone temper was common in the Late Woodland period (AD 400 - 900) and in the American Bottom of Western Illinois during the Emergent Mississippian period (AD 750-1000). A test of performance characteristics revealed that the samples with limestone temper were significantly more resistant to mechanical stress than are grit or grog tempered replicas fired to 600°C.(4) Calcareous ancient ceramics were also found in the Iron Age storage jars which were excavated at Tel Hadar on the eastern shore of the sea of Galillee. The study revealed that the potter had used calcareous raw materials for the preparation of storage jars in order to allow for low sintering temperature (700-800°C)(10, 11) showed that an increase of the flexural strength from 7 to 17 MPa was obtained by adding 15 % of calcite when clay and calcite mixture was sintered at 1000°C. Other studies found that sawdust, marble and granite could be added in clay material(9, 1, 3,) and that the additives act as a fluxing agent, reducing the sintering temperature of the clay materials. The aim of this work is to study the effect of adding the limestone dust from the limestone grinding mill into Angthong pottery clay.

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Experimental procedure

Local area pottery clay from Angthong province was used in this study. Limestone dust from a limestone grinding mill was sieved through a 35 mesh stainless steel sieve. The chemical composition of clay and limestone dust was characterized by X-ray fluorescence (XRF), Oxford ED2000. The mineralogical composition was measured by X-ray diffraction (XRD), Philips PW3710 diffractometer (CuKα radiation). The particle size distribution was measured by laser particle size analyzer (Mastersizer Malvern S). Mixtures containing 0, 10, 20, 30, 40, and 50 wt% of limestone dust were prepared by mixing with water and were aged for 1 day. The mixtures were kneaded by hand until they were soft enough to form cylindrical bars by extrusion. The specimens were measured for their weights and lengths after extrusion and after drying in order to calculate the moisture content and linear shrinkage using the relationship $\Delta L/L$, where ΔL is the change in length of the dried specimens and L is the original length of the wet specimens. Dried test bars were sintered at different temperatures (600, 700, 900 and 1000°C) for 1 h, with a heating rate of 3°C/min. The mechanical strength of sintered samples (average of five specimens for each value) was measured with a universal testing machine (Instron Universal Tester 5583) in a three-point bending test at a constant ramp rate of 2.27 lbf/min. Water absorption was measured by a water displacement method following ISO 10545-3 standard. Linear firing shrinkage uses the relationship $\Delta L/L$, where ΔL is the change in length of sintered specimens and L is the length of the dried specimens. Fracture surfaces were observed by scanning electron microscope (SEM), Philips XL 30CP. Ca mapping was detected by SEM with EDX, Jeol 6400.

Results and discussion

The chemical composition of clay and limestone dust are indicated in Table 1.

Similar to common pottery clay, Angthong clay presents a typical composition which mainly consists of SiO_2 and Al_2O_3 as major oxides where Fe_2O_3, Na_2O and K_2O and CaO are minor components. The main composition of limestone dust is CaO, which is detected after calcination at 1000°C. Less than 10% of SiO_2 and Al_2O_3 is found in limestone dust.

Figure 1 and Figure 2 show the X-ray diffraction patterns of the clay and limestone dust. It can be noted that the clay material is constituted by quartz, kaolinite, illite and smectite. The limestone dust contains calcite as a major phase and quartz as a minor mineral. LOI of limestone dust is almost 40% because of decomposition of $CaCO_3$ to CaO and CO_2.

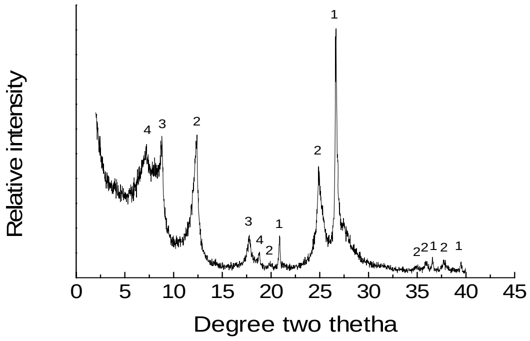


Figure 1. XRD pattern of Angthong pottery clay by orientation method (Note : 1 = quartz, 2 = kaolinite, 3 = illite, 4 = smectite).

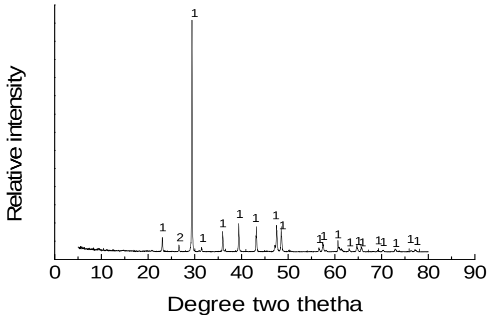


Figure 2. XRD pattern of limestone dust (Note : 1 = calcite, 2 = quartz).

Table 1. Chemical composition of the raw materials as determined by XRF (wt%).

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	MgO	K_2O	CaO	LOI 1000°C
Clay	58.78	24.17	2.73	0.42	0.32	0.05	1.29	0.31	11.93
Dust	4.75	2.48	0.79	0.12	nil	0.58	0.06	49.85	40.44

Result from the Mastersizer, Figure 3, shows the particle size distribution of the clay and limestone dust. The graph presents substantial difference of particle size distribution between clay and limestone dust where particle size of limestone dust is much coarser than clay. More than 70% of clay is smaller than 0.2 µm, the rest is in the range of 0.2-40 µm. Only 15 % of limestone dust is smaller than 10 µm and 70% is in the range of 10-250 µm. Although the limestone was passed through a 35 mesh stainless steel sieve, its average size (150 µm or 0.15 mm) is smaller than coarse sand. Normally, average size of coarse sand used in Angthong pottery is about 0.5 mm.

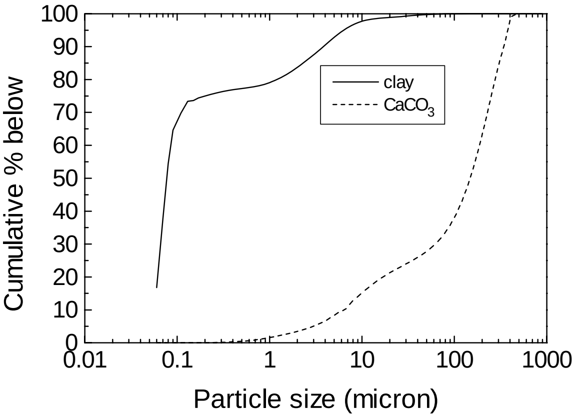
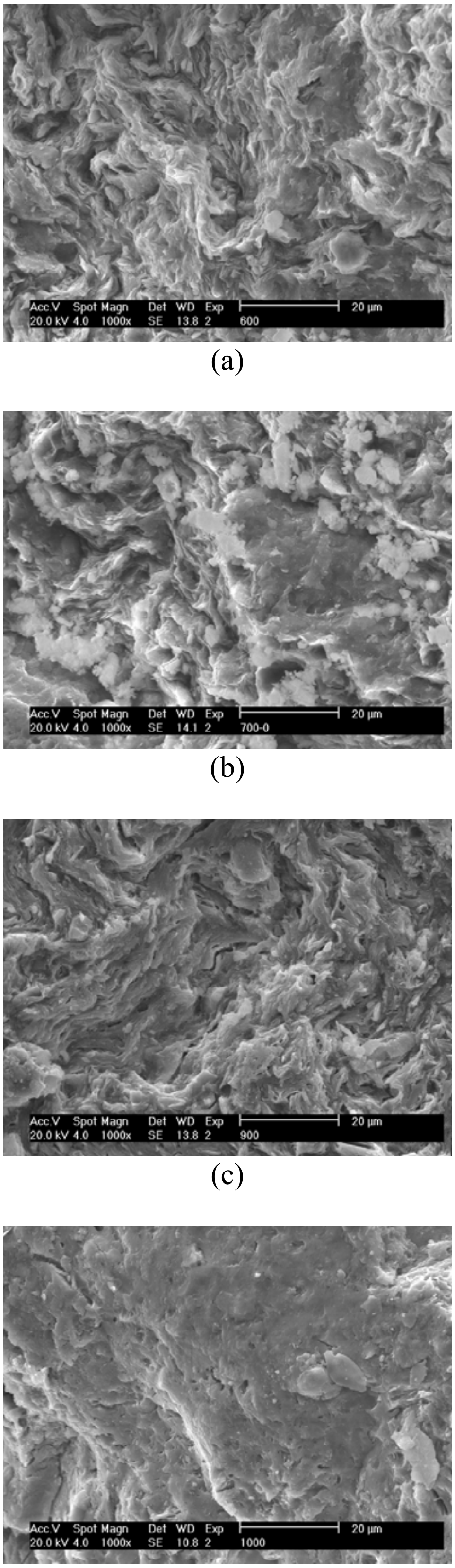


Figure 3. Particle size distribution of the raw materials.

Before mixing limestone dust as an additive, the densification behavior of samples sintered between 600-1000°C was studied in terms of water absorption, linear firing shrinkage, phase formation, microstructure and flexural strength. The sintering temperature at 800°C is not chosen for this experiment because it is close to the decomposition point of $CaCO_3$ which is about 825°C.(6)

The SEM micrographs reveal fracture surfaces of samples without limestone dust sintered at various temperatures as shown in Figure 4. At 600°C and 700°C (Figure 4 (a) and Figure 4 (b)), the surface is rough and porous and small isolated particles are also found. At 900°C (Figure 4 (c)), smaller pores and well-bond aggregates are shown clearly. At 1000°C (Figure.4 (d)) the porosity is reduced when the surface is smooth and the structure is dense.



(a)

(b)

(c)

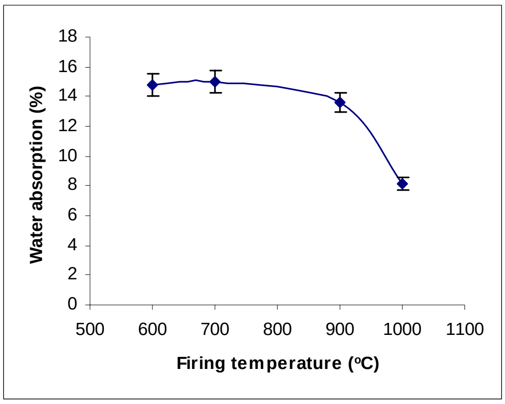
(d)

Figure 4. SEM micrographs of samples without limestone dust sintered at (a) 600°C, (b) 700°C, (c) 900°C and (d) 1000°C for 1 h.

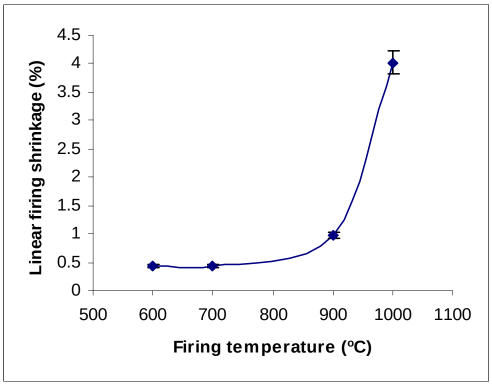
Figure 5 (a) shows the water absorption curve of samples without limestone dust sintered at different temperatures. The water absorption values decrease significantly at 1000^{o}C which is almost 7 % lower than that of the samples sintered at 600^{o}C and 700^{o}C. Slightly different values are found in the samples sintered between 600-900^{o}C.

The linear firing shrinkage of samples is presented in Figure 5(b). It could be noticed that samples fired between 600-900^{o}C show very low shrinkage (< 1%) because the densification mechanism in this step results from surface diffusion.(5) In accord with Brazilian kaolinitic clay,(7) high linear firing shrinkage of 4%, can be obtained after firing at 1000^{o}C.

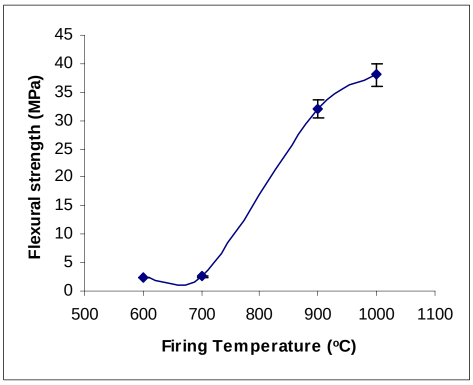
The mechanical strength of the specimens was examined in terms of flexural strength (Figure 5(c)). Samples sintered at 900^{o}C and 1000^{o}C show much higher strength value than samples sintered at 600^{o}C and 700^{o}C. This is the result of a difference in the densification progress between low firing temperatures (600^{o}C and 700^{o}C) and higher firing temperatures (900^{o}C and 1000^{o}C) as shown in the SEM micrographs.



(a)



(b)



(c)

Figure 5. Changes in the most relevant properties : (a) water absorption, (b) linear firing and (c) flexural strength, of sintered samples without limestone dust, as a function of sintering temperatures.

The green samples mixed with limestone dust were characterized for water content and shrinkage after drying as shown in Figure 6 and Figure 7. The water content was measured in terms of weight loss after drying. Increasing the amount of limestone dust content could decrease water content in green bodies, especially for 40 and 50 wt% limestone content. This behavior is related to the higher limestone dust content because limestone dust does not adsorb water like clay. As expected, the shrinkage of samples after drying is reduced when limestone dust content increases because the drying shrinkage results from water evaporation from green bodies. Therefore, low water content in green bodies gives rise to low shrinkage after drying.

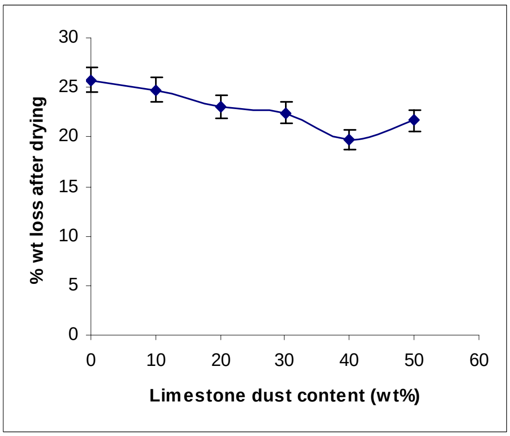


Figure 6. Water content in green specimens with 10, 20, 30, 40, and 50 wt.% of limestone dust content.

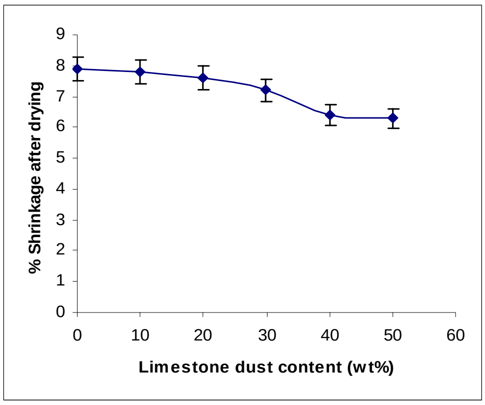
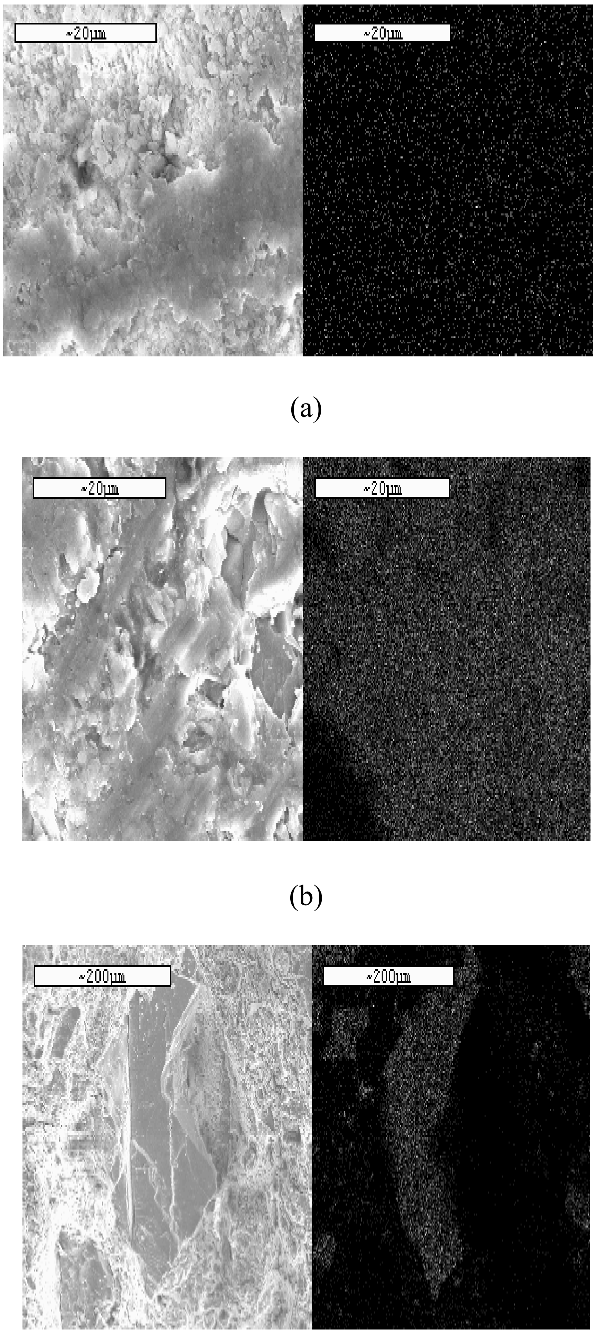


Figure 7. Shrinkage after drying of green specimens with 10, 20, 30, 40, and 50 wt. % of limestone dust content.

The samples were divided into 2 groups. The first group was fired at 600°C and 700°C and lime blowing did not occur while another group was fired at 900°C and 1000°C and lime blowing occurred gradually after the samples were left in air. Compared to Traoré's experiment,(11) pottery clay from Burkina Faso mixed with 15 % of calcite formed anorthite phase after sintering at 1000°C for 15 min. It is probable that calcite used in Traoré's experiment is very fine, <2 µm. Therefore it could be easier for CaO to form a new phase by reacting with SiO_2 and Al_2O_3.

Because of lime blowing in samples with limestone dust fired at 900°C and 1000°C, these samples do not have to be tested for physical properties. Only the samples with limestone dust fired at 600°C and 700°C were tested.

The SEM micrographs with EDX mapping results reveal fracture surfaces and limestone distribution of samples without and with 50% limestone dust fired at 700°C for 1 h as shown in Figure 8(a) and Figure 8(b). The samples with limestone dust show dense Ca content as white spot distributed in the whole area (Figure 8(b)). With EDX spectrum applied, Figure 9(a) and Figure 9(b) confirm the concentration of Ca in the specimens in so far as samples with limestone dust show a higher peak of Ca. However, large particles of limestone were also detected (Figure 8 (c)). The distribution of limestone dust in these specimens is useful information to imply packing density. Because there are two different size distributions of clay and limestone dust, the particle packing density of samples with limestone dust should be different from samples without limestone dust. The coarser limestone particles allow the fine clay to fill the interstices between the coarse particles.

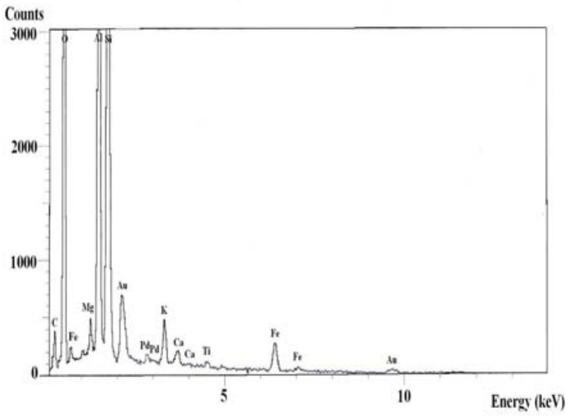


(a)

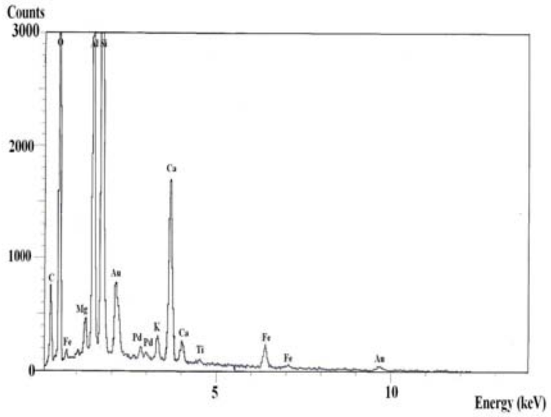
(b)

(c)

Figure 8. SEM micrographs and EDX mapping of samples (a) without limestone dust (b) and (c) with 50 wt.% of limestone dust, sintered at 700°C for 1 h.



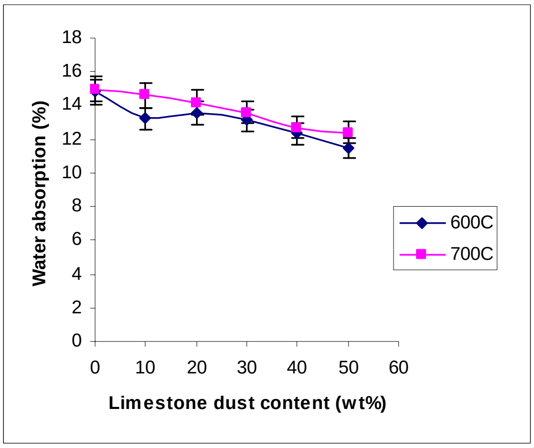
(a)



(b)

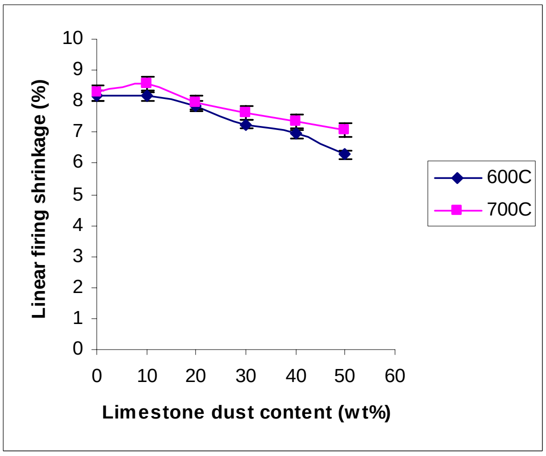
Figure 9. EDX spectrum of samples (a) without limestone dust and (b) with 50% of limestone dust, sintered at 700°C for 1 h.

Figure 10(a) shows water absorption of samples with various amount of limestone dust contents when the samples were sintered at 600°C and 700°C. Increasing the limestone dust content could reduce the water absorption value of samples. Especially for the samples with 50% limestone dust content, water absorption value is about 3% lower than that of the samples without limestone dust. It is possible that limestone particles are not as porous as partially sintered bodies of clay. So the water absorption values of samples with limestone dust are lower. Slightly different water absorption values were noticed when the samples were sintered at different temperatures. That means sintering temperature does not affect the water absorption results. As mentioned in the previous results, surface diffusion is the densification mechanism for samples sintered between 600-900°C. Surface diffusion does not result in shrinkage of the compact and a decrease in porosity.(5)



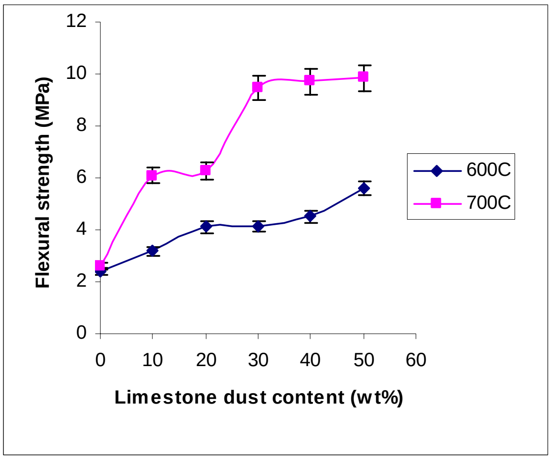
(a)

Figure 10(b) shows linear firing shrinkage of the samples with limestone dust. Similar to water absorption results, the linear firing shrinkage decreases when limestone dust content increases. At 50% limestone dust content, for example, the shrinkage is about 2% lower than that of the samples without limestone dust. Normally, firing shrinkage can be substantially decreased by addition of nonshrinking material to the mix.(5) In this case limestone dust behaves like nonshrinkage material.



(b)

Figure 10 (c) shows flexural strength of the samples with limestone dust. At the same limestone dust content, samples fired at 700°C are stronger than those fired at 600°C because a higher temperature promotes a stronger driving force for densification. Considering the effect of limestone dust content on flexural strength, the samples are stronger when limestone dust content increases. Evaluating the particle size distribution and EDX mapping results, limestone dust is much bigger than clay. Therefore higher limestone dust content provides a higher amount of large particles in the mixture of clay and limestone dust. According to(9) any mixture of particles of different sizes should reach a higher packing density than that of individual components. In our case, packing density plays an important role to determine flexural strength of samples with limestone dust.



(c)

Figure 10. Changes in the most relevant properties : (a) water absorption, (b) linear firing shrinkage and (c) flexural strength, of sintered samples with 10, 20, 30, 40, and 50 wt.% of limestone dust content, sintered at 600 and 700°C for 1 h.

The highest strength was obtained from samples with 50% limestone dust. In comparison to samples without limestone dust, adding limestone dust improved strength from 2.4 MPa to 9.8 MPa. According to specimens after breaking, black coring was found in the center of each sample without limestone dust fired at 600°C and 700°C. It is possible that black coring is a major cause for lowering the flexural strength. In fact, black coring is a problem for iron-bearing clay when body carbon fails to oxidize to CO_2 and takes oxygen from Fe_2O_3 (reducing it to FeO, a powerful flux). This FeO will then flux the body, sealing it and preventing the escape of remaining carbon in the body.(8, 2) Adding limestone dust in this experiment leads to a complete disappearance of black coring because large limestone particles provide space between limestone particles; therefore oxygen could diffuse easily into clay which fills in the interstices between limestone particles. Unlike samples without limestone dust, packing of fine clay particles may provide smaller interstitial pores. In the case of Angthong province, the normal firing temperature is about 900°C because black coring is also found if the firing temperature is lower.

Conclusions

The results obtained in this work show that limestone dust content up to 50 wt% can be incorporated into clay causing its mechanical properties. The flexural strength increased from 2.4 to 9.8 by adding 50 wt.% of limestone dust when the samples were sintered at 700°C for 1 h. Furthermore, using limestone as an additive can eliminate black coring. There are at least six benefits of incorporating limestone dust into clay :

(1) low water content in green bodies makes it easy to dry
(2) decreasing water absorption
(3) low shrinkage and absence of black coring of sintered bodies
(4) increasing flexural strength of sintered bodies
(5) reduced clay consumption and finally
(6) saving energy for firing.

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