# GREEN BRICKS

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## 1. Introduction

The objective of this study is to demonstrate that oyster-shells can be reused as construction materials (red brick), based on their chemical and mechanical properties. This study aimed to find the ways to effective use such a large amount of oyster-shell (OS) through reuse. The experiment added oyster shell powder into the clay in different ratios, and observed the sintering characteristics, microstructure and mechanical properties of the samples.

## 2. Design Concept

South Taiwan is an important oyster producing area, the oyster shells abandoned is about 160,000 tons per year. For the purpose, how to use oyster shells to become a valuable materials. In this study, different proportions of oyster shell powders ($CaCO_3$) were added into the clay (brick), and these samples were sintered at temperature ranging from 775 °C to 900 °C. The microstructure, density, shrinkage rate and the hardness of sintered ceramics were observed and analyzed. When the bricks with 50 wt.% oyster addition sintered at 825 °C, it can effectively reduce the sintering temperature and improve the brick density. The hardness for the 50 wt.% oyster-doped bricks sintered at 825 °C was found to be 415 Hv, and the bulk density = 2.56 g/cm$^3$, but the brick color become light. In addition, the hardness for the 20 wt.% oyster-doped bricks sintered at 900 °C was found to be 305 Hv, and the bulk density = 2.30 g/cm$^3$, however,the sintered ceramics can be maintained at red color. For undoped bricks, it has to be sintered at 950 °C, and the hardness is 180 Hv only.

## 3. Technical Development

Figure 1 shows the composition analysis of the initial raw material of clay. A clay sample of normal bricks was obtained from a local brick manufacturing plant. According to XRD analysis, the essential components of clay were $SiO_2$ with a small amount of $Na(AlSi_3O_8)$, $Fe_2O_3$, $(Mg_{0.25}Fe_{0.75})$ $(Ca_{0.04}Fe_{0.96})(SiO_3)_2$. The composition of clay changed slightly after sintering, but the main phase was still $SiO_2$. X-ray diffraction analysis (XRD) was carried out to investigate the properties of oyster-shell for raw materials. Various oyster-shells due to sources and individual characteristics are almost similar in the chemical composition. The mineral phase of calcium carbonate turns out to be calcite as shown in Figure 2.The shell ends up being 96 percent calcium carbonate, a very hard, chalky substance. Other trace minerals in the shell include silicon, magnesium, sulfate, phosphorus, sodium, strontium.  Figure 3 shows the XRD analysis of composition with different contents of oyster shell powder sintering at 825°C.According to JCPD comparison,the composition was $SiO_2$, $Mg_2SiO_4$,$Ca_2Fe_2O_5$,$(Mg_{0.46}Fe_{1.537})Si_2O_6$, $Ca_2MgSi_2O_7$. It was observed in the XRD chart that a larger addition of $CaCO_3$ makes the $Ca_2Fe_2O_5$ more obvious, thus producing $(Mg_{0.46}Fe_{1.537})Si_2O_6$ phase.As we know,the $CaCO_3$ resolved into CaO and $CO_2$ at 800°C, and the CaO reacted with clay, so the addition of oyster shell powder generated $Ca_2Fe_2O_5$ phase.

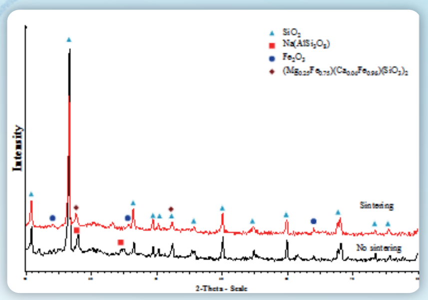


**Fig. 1** *The phase constitutes of raw materials and sintered bricks.*

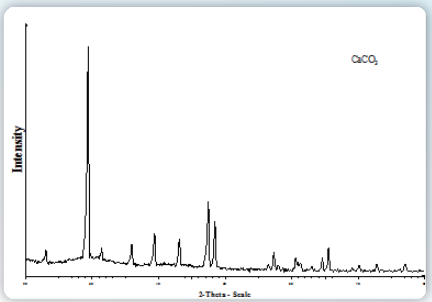


**Fig. 2** *The XRD pattern of the oyster-shells*

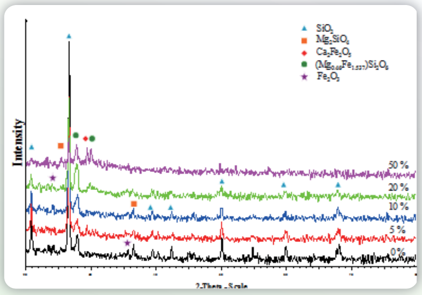


**Fig. 3** *The phase constitutes of clay with different amount of oyster-shell sintered at 825℃.*

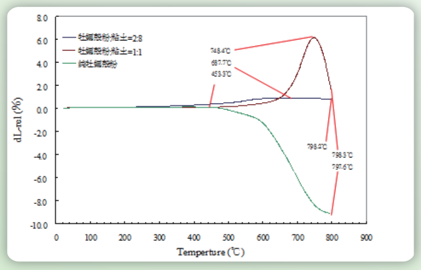


**Fig. 4** *The effect of temperature on the shrinkage rate of clay with different amount of oyster-shell.*

Figure 4 shows the TMA analysis of clay mixed with oyster shell powder in different ratios. The pure oyster shell powder began to shrink at 453.3°C,and the shrinkage was more obvious at 600~800°C, possibly because the $CaCO_3$ resolved into CaO and $CO_2$ at 600°C ~800°C,and the $CO_2$ dissipated into the air,so that the oyster shell powders were shrank obviously.When the ratio of oyster shell powder to clay was 1:1 and the temperature was 750°C, the brick was expanded obviously, whereas there was no obvious difference when the ratio of oyster shell powder to clay. This was because the addition of 50 wt.% resulted in a new phase of $Ca_2Fe_2O_5$ as shown in the XRD analysis (Fig.2 and Fig.3),so that the sample was expanded.

The sintering temperature of traditional bricks was above 900°C, which wastes resources and increases the product cost.The oyster-shell powders added into clay with different amount in this experiment. Figure 5 shows the microstructures of clay at different sintering temperatures and in different ratios of oyster-shell powder.The microstructure pictures that the sintering was denser when the ratio of oyster-shell powder into clay was 1:1 and the temperature was higher than 825°C, as shown in Figure 5 (b). When the specimens were sintered at 800°C, regardless of the amount of oyster-shell powder added, the specimen seem to be undensification, as shown in Figure 5 (a). Because the melting point of CaCO3 was 825°C, the low temperature oyster-shell powder was added in the brick to form liquid-phase sintering to reduce the sintering temperature of brick and increase the density of brick. If the addition of oyster-shell powder is lower than 50 wt.%, the brick cannot be densed even at the sintering temperature of 900°C, as shown in Figure 5 (c) and 5 (d). From microstructure point of viewing, the best ratio of CaCO3 to clay is 1:1,since lower sintering temperature and higher bulk density can be obtained.

The bricks made with clay normally have a bulk density of 1.8–2.0g/cm$^3$.[7] The measurements of bulk density for different proportions of oyster-shell powder fired at four temperatures are demonstrated in Fig. 6. As shown, the bulk density of the bricks is proportional to the quantity of oyster-shell powder added in the mixture. When the content of oyster-shell powder was 50 wt.%, the

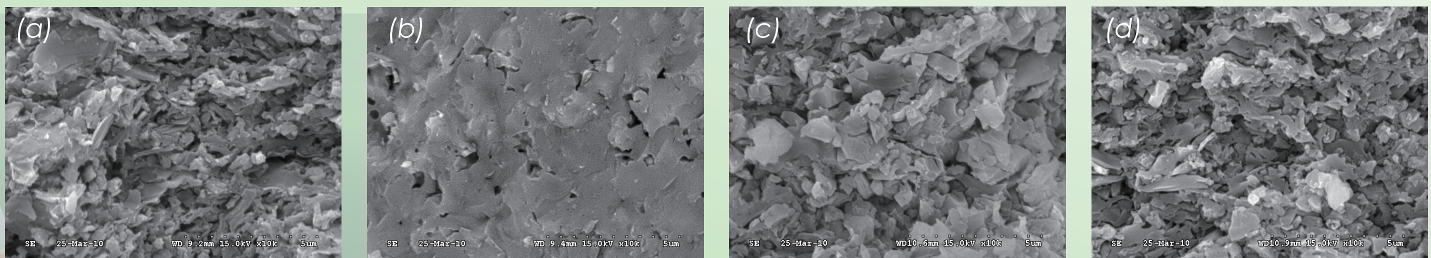


**Fig. 5** *The SEM microstructures of clay at*

*(a) 800℃/50wt.%OS (b) 825℃/50wt.%OS (c) 900℃/0wt.%OS (d) 900℃/20wt.%OS*

density of brick increased with the sintering temperature. The increase in the content of oyster-shell powder and in the sintering temperature was helpful to increase the brick density.

According to the experimental result, the sintering can be finished when the ratio of clay to oyster shell powder is 1:1 and the sintering temperature is 825°C, and the density of red brick can be increased. The mechanical properties of red brick are evaluated by hardness testing, so as to observe whether the addition of oyster shell powder to the clay can increase the hardness of red brick. The sintering temperature of conventional red bricks is > 900°C, and the hardness value is about 169.72 Hv. Figure 8 shows the hardness test of addition of different contents of oyster shell powder and sintering temperature, the result shows that when the sintering temperature is above 825°C,the hardness value of red brick increases with the content of oyster shell powder. According to the microstructure analysis, when the sintering temperature is lower than 825°C, the addition of 50 wt.% oyster shell powder cannot be sintered well, so the hardness value is very low about 116.08 Hv. The sintering temperature of brick can be reduced and the mechanical property of brick can be increased when the 50wt.% oyster shell powder were added into the clay . Figure 8 shows the sintered bricks with different addition of oyster shell powder , the color inclines to white when the addition is 50 wt.% oyster shell powder, if the addition of oyster shell powder is reduced to 20 wt.%, the red brick can keep in red.

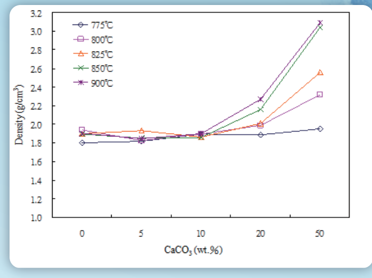


**Fig. 6** *The relationship of density vs oyster-shell amount for the clay sintered at differentsintering temperature.*

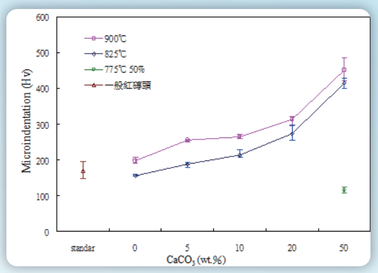


**Fig. 7** *The relationship of micro-hardness vs oyster-shell amount for the clay sintered at different sintering temperature.*

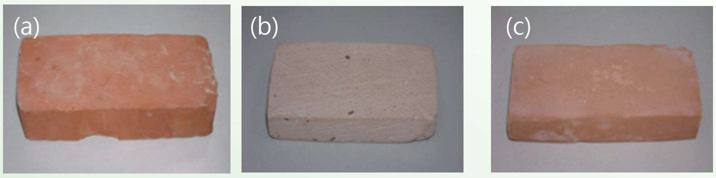


**Fig. 8** *(a) Conventional brick*
*(b) brick with 50 wt.% OS addition*
*(c) brick with 20 wt.% OS addition*

## 4. Technological Competitiveness

When 20 wt.% oyster shell powder ($CaCO_3$) was added into the clay and the sintering temperature was at 900 °C, the sintering temperature could be reduced and the density could be increased effectively. In addition, the microstructure was denser than that of traditional red bricks. The manufacturing cost of bricks and the environmental pollution could also be reduced. The clay with 50 wt.% $CaCO_3$ added at 825°C, the hardness was 415.42 Hv, the brick density was 2.56 g/cm$^3$, and the color of brick became light. The clay with 20 wt.% oyster powder added and sintered at 900°C, the hardness was 305 Hv, the sintered density was 2.30 g/cm$^3$, and the brick can maintain the red color.

## 5. R&D Result

In this study, when 50 wt.% oyster shell powder ($CaCO_3$) was added into the clay and the sintering temperature was above 825°C, the full densification of bricks were obtained.It means the sintering temperature could be reduced and the brick density could be increased effectively.The oyster shell powder added bricks were denser than that of traditional red bricks sintered at 900°C.The manufacturing cost of bricks and the environmental pollution could also be reduced. The clay with 50 wt.% $CaCO_3$ at 825°C, the hardness was 415 Hv, the brick density was 2.56 g/cm$^3$, and the color of brick became light. The clay with 20 wt.% oyster powder at 900°C, the hardness was 305 Hv, the brick density was 2.30 g/cm$^3$, and the red brick maintained the red color. In comparison to the brick without oyster shell powder, the sintering temperature should be at above 950°C, the hardness was 180 Hv, and the sintered density was 2.30 g/cm$^3$.