

Effective Treatment Technique for Producing a Highly Pozzolanic Clay in a Construction Work

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ABSTRACT: A high reactivity pozzolanic clay was developed in this work as a partially replacing cement material for eco-friendly construction. Kaolinite clay was treated at a transformation temperature range of meta-kaolin formation for 6 h in a simple electric furnace. The heated kaolinite clay was separately cool down with 2-different techniques, a normal cool down using a free-cooling rate and a quenching cool down, to make an active phase in a pozzolanic activity. The pozzolanic activity of the treated kaolinite clay was evaluated via the Frattini test, and the compressive strength of the treated clay-cement mixed samples was reported. In comparison to the normal cool down technique, the quenching cool down technique in the heat treatment process generated a higher reactivity clay with a higher degree of reactive metakaolin phase. The Frattini test revealed a decrease in Ca^{2+} and OH^- ions in the $\text{Ca}(\text{OH})_2$ solution, which confirmed the pozzolanic reaction between the $\text{Ca}(\text{OH})_2$ and the high reactive kaolinite clay from the quenching technique. The replacement of cement with a highly reactive pozzolanic kaolinite clay effectively enhanced the compressive strength above the standard requirements within 2-days curing. Also, the compressive strength of the treated clay-cement mixed samples after 2-days curing was comparable to the strength after 7-days curing of the cement samples. This study thus revealed a new effective technique to produce a high potential clay as a cement replacement material in the construction works.

KEYWORDS: Pozzolanic materials, Kaolinite clay; Cooling treatment technique, Compressive strength, Construction.

1. INTRODUCTION

Ordinary Portland cement is the most widely used material in construction works. When Ordinary Portland cement is mixed with water, a hydration reaction between cement and water takes place generating calcium silicate hydrate (CSH) as a main product resulting in a hardened matter (Murat, 1983). However, In Ordinary Portland cement manufacturing, a lot of fuel and high energy $\sim 1400^\circ\text{C}$ are consumed and a large amount of carbon dioxide (CO_2) is released causing an environmental problem (Toniolo and Boccaccini, 2017; Sabir et al., 2001; Peter and Martin, 2006). To overcome this problem, cement replacement materials become an attractive research topic not only under the economic concept but also the eco-friendly materials and technologies in construction.

Pozzolanic material is Al_2O_3 and SiO_2 enriched material with a low cementitious value itself. However, Al_2O_3 and SiO_2 in pozzolanic materials can chemically react with calcium hydroxide ($\text{Ca}(\text{OH})_2$), a product of a hydration reaction between cement and water, and forms calcium silicate hydrate (CSH) or calcium aluminate hydrate (CAH) for hardening cement (ASTM C618 2013; Meller et al., 2007). This reaction is called “a pozzolanic reaction”, which is relatively similar to a hydration reaction in the cement but the reaction rate is slower. There are many pozzolanic materials such as silica fume, fly ash, rice hush ash, granulated blast furnace slag, and heat-treated kaolin (Liu et al., 2017; Chakchouk et al., 2009; Donatello et al., 2010). The most recently attractive pozzolanic material among these materials is heat-treated kaolinite clay which is produced via thermal treatment resulting in a consistently qualified property (Ma et al., 2018).

Heat-treated kaolinite clay is prepared by heating the kaolinite clay at a certain temperature to form a reactive phase in the kaolinite structure. In a heat-treatment process, the chemical water in the kaolinite clay structure is removed under the temperature around $450 - 850^\circ\text{C}$, in which the kaolinite crystalline phase is transformed into a metastable phase called “metakaolin” with high contribution to a pozzolanic reaction (Tironi et al., 2013; Tironi et al., 2014). When reactive metakaolin in heat-treated clay reacts with $\text{Ca}(\text{OH})_2$, CSH and CAH are produced for bonding other components and increasing the cement strength (Sayamipuk, 2000; Salvador, 1995). Heat-treated kaolinite clay is thus used as a cement replacement material in concrete to obtain higher density and strength (Sabir et al., 2001).

However, the metakaolin phase is relatively unstable under the formation temperature, in other words, the metakaolin phase is transformed into $\gamma\text{-Al}_2\text{O}_3$, cristobalite (SiO_2), and primary mullite crystals (Salvador, 1995; Habert et al., 2008; David et al., 2017). To preserve the reactivity of the metakaolin phase, a new effective cooling technique of heat treatment that has never been done so far was proposed to control the amount and quality of metakaolin and maintain a pozzolanic reactivity in heat-treated kaolinite clay in this study. This is not only a challenge for proposing a new process, but also enhancing the efficiency of alternative construction materials. Kaolinite clay was heat-treated at 450°C and 500°C , according to the study of their thermal behaviors, using normal cool down technique and quenching cool down technique. The pozzolanic reactivity of heat-treated kaolinite clay related to the strength in a partially replacing cement sample was determined. The effective technique and performance of treated kaolinite clay as a sustainable cement replacement material were investigated and reported for usable construction.

2. MATERIALS AND METHODS

2.1 Raw Materials and Characterization

Kaolinite clay used in this study is imported from China by the Lucky Union Company. The clay was dried at 100°C for 24 h before sieving through a 325-mesh stainless steel sieve. X-ray fluorescence spectrophotometer (XRF: Rigaku ZSXPrimus IV) was used to examine the chemical composition of kaolinite clay in which is reported in Table 1. The mineralogical composition of kaolinite clay was determined by X-ray diffraction diffractometer (XRD: Bruker D8 ADVANCE) with Cu-K_α radiation at 40 kV and 40 mA. The step size was 0.02° in 0.2 sec over scanning range 2θ from 5 to 60° with step width 2°min^{-1} . Thermogravimetric analysis was performed on a STA449F3 simultaneous thermal analyzer (Netzsch, Germany). The sample was heated in alumina (Al_2O_3) crucibles from 35°C to 1200°C with a heating rate of $10^\circ\text{C min}^{-1}$ under an O_2 atmosphere.

2.2 Thermal-Cooling treatments and characterization

Kaolinite clay was treated at 450°C and 500°C with soaking time for 6 h in which dehydration and metakaolin transformation take place, according to the preliminary result of thermal analysis shown

in Figure 1, and the literature reviews (Sabir et al., 2001; David et al., 2017; Tironi et al., 2012). The cooling step was divided into two techniques. The first cooling technique was performed using a free-cooling rate in the normal electric furnace. The second cooling was done by a quenching technique in which the kaolinite clay was suddenly taken out of the furnace once the soaking time was finished (Figure 2). Then, the phase transformation of both thermally treated kaolinite clay was examined by the XRD technique.

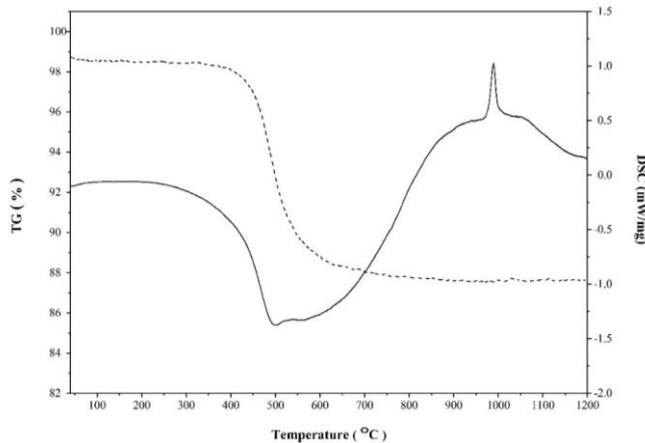


Figure 1 TGA (dashed line) and DSC (solid line) curve of the kaolinite clay

2.3 Pozzolanic Activity of Treated Kaolinite Clay

Pozzolanic activity of treated kaolinite clay was evaluated via the pozzolanic reaction test and compressive strength test (Sayamipuk, 2000). The Frattini method was performed according to the procedure described in the ASTM C311 standard for the pozzolanic reaction test. 5-g treated kaolinite clay was mixed with 2-g calcium hydroxide and 10 ml distilled water in a beaker and then covered with plastic wrap. The mixture was kept at a temperature of 38 °C for 2 days and 7 days. After curing, the pozzolanic reaction of the cured samples was evaluated using an inductively coupled plasma optical emission spectrometer (ICP-OES) and HACH HQ430d conductivity meter.

2.4 Compressive Strength Test

The compressive strength of the treated kaolinite clay was determined according to ASTM C109. The sample was prepared using water to cement (w/c) ratio of 0.4 with 20-wt% treated kaolinite clay in replacement of cement. The mixtures were homogeneously mixed for 5 minutes before molding in a 50 mm x 50 mm x 50 mm metal mold. The sample mold was wrapped with plastic wrap and kept at room temperature for 24 h. Each sample was detached from the metal mold and continually kept at room temperature for 2 days and 7 days under wraps in plastic wrap. The compressive strength values of the cured samples were determined using a compression machine (ELE, Germany: capacity 200 ton).

3. RESULTS AND DISCUSSION

3.1 Thermal Analysis and Characterizations of Clay

Table 1 shows the chemical compositions of kaolinite clay, in which quartz (SiO₂) and alumina (Al₂O₃) are the main components as expected. The thermal behavior of kaolinite clay is shown in Figure 1. The dehydroxylation of the chemically combined water in the kaolinite clay used was detected in the range of 450 - 600 °C. The kaolinite crystalline phase (Al₂O₃•2SiO₂•2H₂O) was transformed to a reactive metakaolin phase (Al₂O₃•2SiO₂) by the elimination of the OH units. This resulted in the pozzolanic property in the kaolinite clay. From Figure 1, the dehydroxylation of combined water started at 450 °C and reached the maximum degree

of dehydroxylation at 500 °C. This indicates that the 500 °C is as low as possible temperature to obtain the highest metakaolin phase formation as well as the highest pozzolanic reactivity in the treated kaolinite clay. Therefore, the pozzolanic activity test of the kaolinite clay was focused at the two different heat-treatment temperatures (450 and 500 °C) with the fixed soaking time at 6 h. Meanwhile, the pozzolanic activity evaluation was carried out on the treated kaolinite clays with different cooling techniques.

Table 1 Chemical compositions of kaolinite clay
Chemical compositions, (wt%)

SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	Etc.
53	41	4	1	1

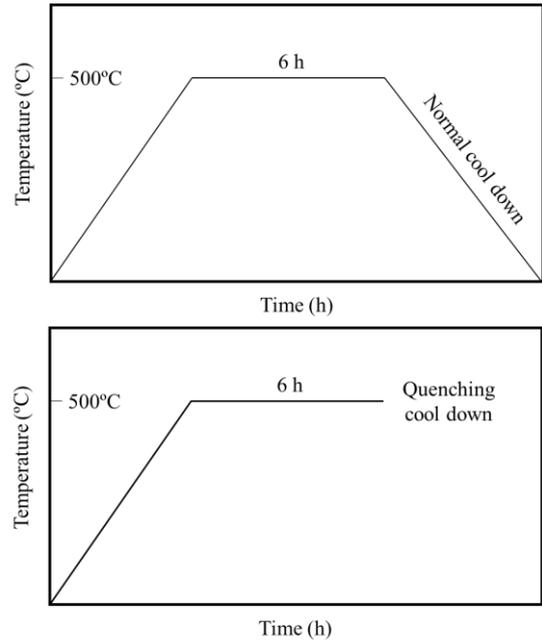


Figure 2 Temperature profiles in thermal-cooling treatments of the kaolinite clay

3.2 Phase Transformation of Clay

X-ray diffractograms of kaolinite clay and treated kaolinite clay are illustrated in Figure 3. The reflection peaks corresponding to kaolinite minerals were obtained as a major phase, while the minor phases of quartz (Q), halloysite (H), and illite (I) minerals were also detected in the kaolinite clay (Figure 3(a)). The X-ray diffractograms of the treated kaolinite clay are shown in Figure 3(b) - 3(e). It was observed that the peaks corresponding to the kaolinite crystalline phase (K) were reduced by increasing heat-treatment temperature. It was due to the kaolinite crystalline phase transformation into the reactive metakaolin phase by the elimination of the OH units (dehydroxylation) after receiving sufficient energy. Reducing peak intensity of kaolinite ($2\theta = 24.83^\circ$) and a slightly different peak intensity of kaolinite and quartz ($2\theta = 26.63^\circ$) also contributed to the enhancement of dehydroxylation when the heat-treatment temperature increased from 450 °C to 500 °C. However, the XRD pattern of metakaolin showed no reflection peak. Instead, a broad hump around $2\theta = 20^\circ$ confirmed the presence of the metakaolin in a metastable amorphous form. Hence, the conversion of kaolinite to metakaolin is confirmed by the absence of its XRD reflections (Souri et al., 2015; Khan et al., 2017).

The amount of the kaolinite crystalline phase showed in Figure 4 was evaluated by Eq. (1), based on the theory reported elsewhere (Ebadzadeh and Ghasemi, 2002; Daou et al., 2020), where I_k and I_q are the peak intensity of kaolinite and quartz, respectively. The peaks at $2\theta = 24.83^\circ$ and 26.63° were also the selected peaks of kaolinite, and quartz used to confirm the phase transformation in the treated kaolinite clay. From Figure 4, the kaolinite crystalline phase was reduced when the heat-treatment temperature increased from

450 °C to 500 °C and using a short period of cooling time of the quenching technique. This suggests that the amount of reactive metakaolin phase was effectively increased in the kaolinite clay after heat treatment at 500 °C and using the quenching cool down technique.

$$\text{Kaolinite crystalline phase} = I_k / (I_k + I_q) \times 100 \quad (1)$$

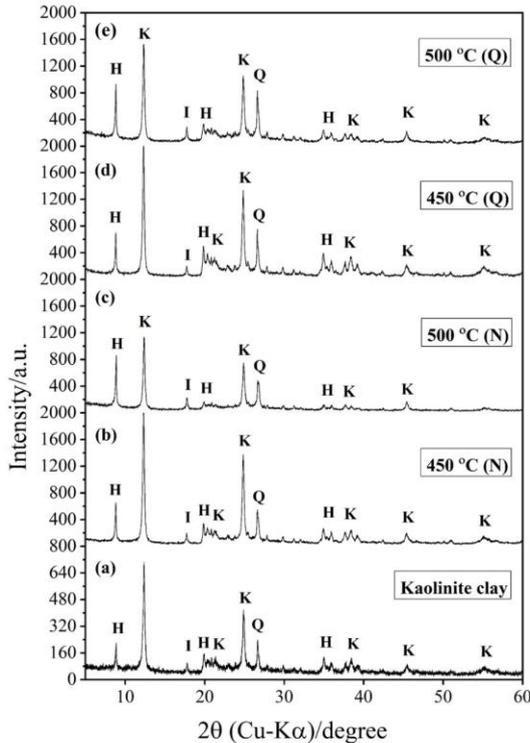


Figure 3 (a) XRD of the kaolinite clay, (b) - (c) treated kaolinite clay (normal cooled down (N)), and (d) - (e) treated kaolinite clay (quenching cooled down (Q))

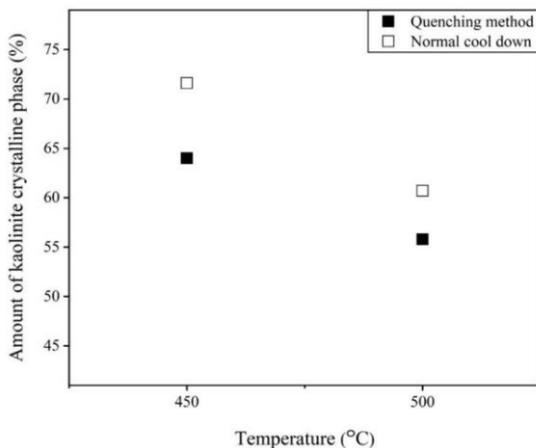


Figure 4 Amount of the kaolinite crystalline phase in the treated kaolinite clay

3.3 Pozzolanic Activity of Clay

The electrical conductivity suggested to the reactivity of the treated kaolinite clay is shown in Figure 5. The curve of the Frattini test (Figure 5(a)) shows the pozzolanic reaction values (dashed line) decreased over time owing to a decrease of Ca^{2+} and OH^- ions in the reaction between treated kaolinite clay and $\text{Ca}(\text{OH})_2$ in the samples (Sayamipuk, 2000). Thus, the position below the dashed line was subjected to the high pozzolanic reactivity based on the residual Ca^{2+} and OH^- ions in the samples. It was clear that the reactivity of the treated kaolinite clay increased with increasing heat-treatment

temperature as well as using the quenching technique, owing to the high degree of reactive metakaolin phase (Tironi et al., 2013; Tironi et al., 2014). In a quenching technique compared to normal cooling, the metakaolin transformed phase presence in a short period at the critical temperature of metakaolin transformation, and also delays the crystallization of $\gamma\text{-Al}_2\text{O}_3$, cristobalite (SiO_2), and primary mullite crystals (David et al., 2017; Tironi, 2012; Rosen et al., 2007). The highly reactive metakaolin phase thus exists in the treated kaolinite clay and increased with a decreased cooling period in a quenching technique. The higher reactive silica and alumina in the reactive metakaolin phase enables enhanced reaction with $\text{Ca}(\text{OH})_2$ and thereby reduced in Ca^{2+} and OH^- ions in the Frattini test.

Therefore, the treated kaolinite clay at 500 °C using the quenching technique showed the highest reactivity in this study. Moreover, the reactivity of the kaolinite clay treated at 450 °C and cooled down by the quenching technique was relatively higher than that of the treated kaolinite clay at 500 °C with the normal cool down technique. From Figure 5(b), the residual Ca^{2+} and OH^- ions in the Frattini test were also analyzed in terms of electrical conductivity. Since Ca^{2+} and OH^- are mobile ions with different charges, they can conduct electricity and become a conducting solution. However, the electrical conductivity values decreased with an increase in heat-treatment temperature. The lower electrical conductivity value was found in the sample obtained from the quenching technique. This was due to the consumption of Ca^{2+} and OH^- ions in the pozzolanic reaction (Habert et al., 2008). This result indicates a higher degree of reactive metakaolin phase and higher pozzolanic activity in the kaolinite clay treated at 500 °C with quenching cool down technique.

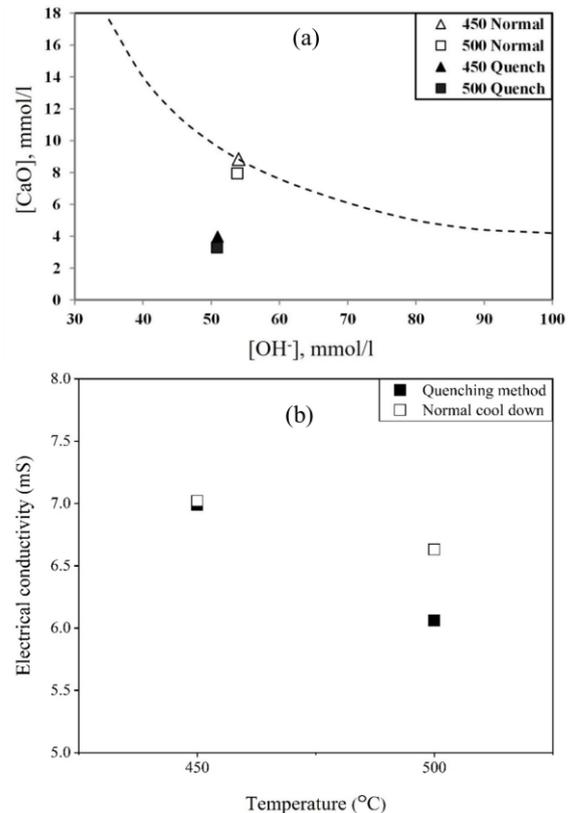


Figure 5 (a) Reactivity of the treated kaolinite clay examined by the Frattini test and (b) The electrical conductivity as the function of heat-treatment temperatures

3.4 Compressive Strength of Treated Clay-cement Samples

The compressive strength of the replaced cement samples with a 20-wt% treated kaolinite clay after curing for 2 days is demonstrated in Figure 6. The compressive strength of these samples was higher than the minimum requirement (19 MPa) of the Portland cement

sample (ASTM C150, 2003; ASTM C150/C150M – 12, 2012). The strength of the partial replacing cement samples with a 20-wt% treated kaolinite clay was developed with an increase of the heat-treatment temperature as well as a quenching technique. The compressive strength after 2-days curing of the cement sample with a 20-wt% quenched kaolinite clay was comparable to the compressive strength after 7-days curing of the cement sample with a 20-wt% normal treated kaolinite clay. This was due to the pozzolanic reaction between the reactive metakaolin phase in the quenched kaolinite clay and the $\text{Ca}(\text{OH})_2$ from the hydration cement sample. Therefore, this study revealed that the high pozzolanic reactivity of the kaolinite clay used as a partial cement replacement material can be achieved by using the quenching cool down technique in a heat-treatment process of the kaolinite clay.

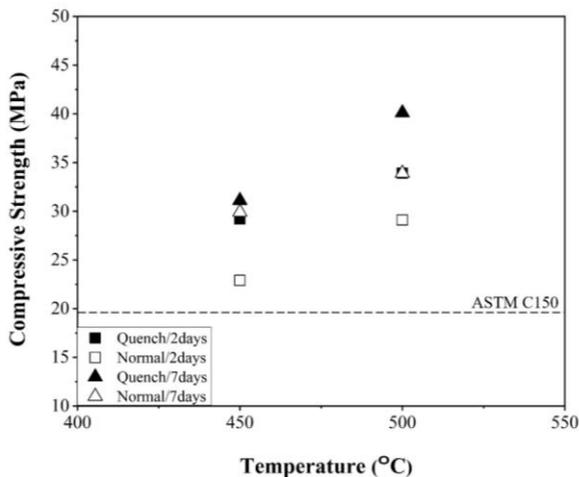


Figure 6 Compressive strength of a 20-wt% treated clay-cement mixed samples

4. CONCLUSIONS

A high reactivity pozzolanic material for use as a partial cement replacement material was produced from kaolinite clay in this study. By using the quenching cool down technique in the heat-treatment process, the pozzolanic reactivity of kaolinite clay was enhanced leading to a highly improved strength of partially replaced cement samples with a highly reactive pozzolanic kaolinite clay. The compressive strength of partially replaced cement samples with 20-wt% treated kaolinite clay was higher than the minimum requirement of Portland cement strength within a short period of 2-days curing. The strength after 2-days curing of the treated clay-cement mixed samples with a quenching kaolinite clay was also comparable to the strength after 7-days curing of the treated clay-cement mixed samples with normal cooling kaolinite clay. This was due to the high pozzolanic reactivity of treated kaolinite clay as a result of the effective cooling technique in a heat-treatment process. The present work reveals an effective technique for reducing costs and environmental impact in the production of high-performance pozzolanic clay in construction works.

5. ACKNOWLEDGEMENTS

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