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Effect of lignite fly ash and rice husk ash ratios on physical properties of lightweight porous geopolymers fabricated by pore-forming agent method

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Abstract - In this study, the porous lightweight geopolymer used lignite fly ash (FA) and rice husk ash (RHA) derived from the local source. The prepared geopolymer slurry was a mixture of FA, RHA, and alkaline solution activators which consisted of Na_2SiO_3 and 10 M of NaOH solution. RHA was applied to replace FA content in the 10-50% ratio by weight. The ratio of solid (fly ash and rice husk ash) and liquid (Na_2SiO_3 and NaOH) is 0.6, while the ratio of Na_2SiO_3 and NaOH is 3. Powder of sponge was employed to create the porous geopolymer materials in 0.5 % by weight. The fresh slurry was poured into cube plastic molds for porous geopolymer casting. Then, the porous geopolymer was cured at 60 oC for 48 hours and 7 days at room temperature. After sintering at 700 oC for 2 hours, the specimens were examined. The micrographs of surface characteristics show an enlarged pore size with increasing RHA amount, corresponding to the % shrinkage/expansion of the specimens. The XRD patterns shows an increase in quartz content by increasing RHA. The water absorption increases with increasing the amount of RHA, related to the porosity. It was found that the amount of RHA can improve the physical properties of geopolymer materials which increases the porosity value when increasing the amount of RHA.

Keywords: Physical properties, fly ash, rice husk ash, porous geopolymer

1. Introduction

The growing demand for infrastructure services causes a high consumption rate of concrete (Benhelal, 2013). As well known, concrete was proceeded by cement playing as the main component. The high temperature in the cement production process releases various environmentally harmful gases, including methane, nitrous oxide, and carbon dioxide (Farhan, 2019), contributing to about 2.8 billion tons of greenhouse gas emissions a year (Malhotra, 2022). For one ton of cement production, 1.5 tons of raw materials were operated and associated with releasing nearly one ton of carbon dioxide gaseous material (Duan, 2015). Thus, clinker-free alternative cementitious materials with higher performance, lower cost, and environmental friendly have required development (Provis, 2015). Inorganic alumino-silicate polymers, referred to as geopolymers, were studied to replace ordinary cement. The chemical process of geopolymerization is prepared by dissolving alumino-silicate materials in an alkaline solution. The reaction reveals an exothermic process and changes amorphous structure to semicrystalline of a three-dimensional alumino-silicate network (Davidovits, 2011). The process has a low carbon footprint and also operates at ambient temperature. In addition, the alumino-silicate precursor was easily found both natural materials (kaolinite, metakaolin, and clays (Davidovits, 2011) (Yip, 2008) and secondary industrial products (fly ash, blast furnace slag, and silica fume (Nath, 2014), (Thokchom, 2011). Geopolymer has been widely studying performance because their properties exhibit improved properties in comparison with portland cement, as follows: excellent mechanical strength (Rashad, 2013), low shrinkage (Duxson, 2007), acid resistance (Pacheco-Torgal *et al.*, 2012), and high-temperature endurance (Pan, 2009).

The advantage of geopolymer, thus, not only dense geopolymer bulk is interested in improving its performance, but lightweight porous geopolymer is also simultaneously developed for applying in thermal insulation (Bai, 2017), wastewater treatment (Bai, 2017), and fire resistance (Alehyen, 2017). There had been prepared porous geopolymer by various strategies: freeze-casting technique without additional dispersants and binders (Papa, 2015), foamed geopolymers (Kioupis, 2018), saponification/peroxide/gel casting combined method (Bai, 2016), 3D printed templates (Franchin, 2015). These techniques can control pore size to narrow distribution, but the processes use hazardous chemical reagents, complex apparatus, and long processing time, indicating that the forming methods are unsuitable for industrial-scale production. The simple and low operating cost is the pore-forming agent (PFA) preparing method. A pore-forming agent was added to the geopolymer structure before geopolymerization. Cementitious solid was formed in the mold and then heated to eliminate the pore-forming agent and treat the solid. The heating temperature is greater than the melting point of a filled pore-forming agent. The solid agent decomposes to be a gaseous state that leaks out from geopolymer bulk, generating residual pore in geopolymer.

Among alumino-silicate materials, fly ash (FA) is the common alumino-silicate source that was used in fly ash-based geopolymer (FAG) production. FAG with heat curing exhibited a similar engineering performance to ordinary Portland cement (OPC) (Vishwakarma *et al.*, 2016). RHA could be used as alumino-silicate materials because Al, Si, and O were found. Rice husk ash (RHA), a by-product agricultural material, is prepared by firing low-cost precursors. The adding of RHA in FAG can reduce cost and improve the performance of the geopolymer. Vishwakarma *et al.* (2016) confirmed that RHA could be replaced the cement for structural concrete production at suitable replacement percentages. The RHA can form calcium silicate hydrate (C-S-H) gel to avoid any crack and corrosion (Vishwakarma, 2016).

Herein, lightweight porous geopolymer was fabricated through simply the PFA method. The mixture of FA and RHA with varying components was designed as an alumino-silicate source. The polyester sponge was chosen to be the pore-forming agent. The solid specimens were cured and sintered, improving strength and eliminating the sponge. After that, the obtained specimens were examined for their physical properties, including the porosity, water absorption, and X-ray diffraction (XRD). The effect of FA replaced by RHA was discussed in terms of crystallographic structure, microstructure, and physical properties.

2. Materials and methods

This research was divided into three parts as follows:

2.1 Material preparation

Lignite fly ash (FA) (Maemoh powerplant, Lampang province, Thailand) and rice husk ash (RHA, Wat Cholae Phra Ngam Community, Chiang Mai Province, Thailand) are the alumino-silicate material precursor in geopolymer specimen preparation. The precursor powders were sieved to obtain particles below 125 µm. 10 M of NaOH solution was prepared by dissolving sodium hydroxide pellets (Sigma-Aldrich, Germany) in deionized water (DI). A polyester sponge (pore-forming agent) was prepared in powder form. The sponge was digested in wet condition for powder preparation by an electric food grinder for 1 min. The as-grounded sponge was dried at 60 °C for 24 h then repeatedly ground in a dry condition for 1 min.

2.2 Geopolymer fabrication

500 g of alumino-silicate mixtures [fly ash (FA): rice husk ash (RHA)] were assembled with different wt% fraction (100:0, 90:10, 80:20, 70:30, 60:40, and 50:50) and then mixed until homogeneous. The sample of each condition was denoted as FA, RHA-10, RHA-20, RHA-30, RHA-40, and RHA-50, respectively. For an alkaline solution (liquid phase) preparation, the sodium silicate (Na_2SiO_3) to sodium hydroxide (NaOH) ratio was fixed at 3. The mixture of the alkaline solution was stirred for 5 min to reach homogeneity and decrease the temperature of the solution. The weight ratio of the solid phase to the liquid phase is 0.6. Powder of sponge was added to geopolymer slurry in 0.5 wt% of the solid phase. The fresh slurry was cast in plastic molds with a cubic plastic mold shape. The porous geopolymer was cured at 60 °C for 48 hours and placed at ambient temperature for 7 days. Finally, the specimens were fired at 700 °C for 2 hours. The fabricated geopolymers were washed by water for 3 times, removing residual alkaline. The as-prepared specimens were examined by various analytical techniques

in physical properties: crystallographic structure, microstructure, porosity, and water absorption.

2.3 Geopolymer characterization

The crystallographic structure of the geopolymer powders was investigated by X-ray diffraction, on Rigaku model miniflex 600 X-ray diffractometer analyzed a 2θ in the range 10-70° with 0.05° step size. Microstructural analysis of the geopolymers was carried out by stereo microscope technique (ZTX model 3S-2C, China). The samples were prepared to study cross-sectional structure. For the percentage expansion calculation, the dimension of the specimens before and after firing was measured and calculated through the relation in equation 1, which is shown as follows.

$$\% \text{ expansion} = (|L_i - L_f| / L_i) \times 100 \quad (1)$$

Where Li is the initial length (before firing) and Lf is the final length (after firing)

Finally, bulk density, water absorption, and apparent porosity concern the ASTM C 373 procedure (ASTM International, 2006). The specimens were cured at room temperature for 9 days. The sample weight was measured in dry condition, noted as dry weight (W1). The cured samples were immersed in boiling water for 5 hours and continuously immersed at room temperature water for 24 hours. The saturation weight (W2) of samples was measured when samples remained in water. The sample was taken out from a water bath, the moisture on the sample surfaces was removed with a damp cloth and measured weight as a wet mass (W3). The bulk density of samples can be calculated using equation 2. Water absorption and apparent porosity were determined by equation 3 and equation 4, respectively.

$$\text{Bulk density} = [W_1 / (W_3 - W_2)] \times \rho\text{water} \quad (2)$$

Where ρwater is the density of water at the measured temperature

$$\text{Percentage water absorption} = (|W_3 - W_1| / W_1) \times 100 \quad (3)$$

$$\text{Apparent porosity} = [(W_3 - W_1) / (W_3 - W_2)] \times 100 \quad (4)$$

Where W_1 = weight of dried specimen (g), W_2 = weight of wet specimen (g), W_3 = weight in water of specimen (g)

3. Results and discussion

Figure 1 presents XRD pattern of FA and various rice husk ash content of the studied geopolymer for comparison. The XRD pattern of FA, RHA-10, RHA-20, and RHA-30 show the peak of hematite (JCPDS no. 73-0603), calcite (JCPDS no. 83-1762), quartz (JCPDS no. 01-85-0335), and sodium carbonate (JCPDS no. 86-0314). The hematite, calcite, alumina, and quartz phase are clearly observed, which is found in the precursor (FA and RHA). In addition, the sodium carbonate phase is a product of the reaction of calcite and the alkaline solution (NaOH) (Rashidian-Dezfouli, 2017), (Nochaiya, 2010). The intensity of this peak decrease with the rise of the rice husk ash content due to low calcite (CaCO3) in the rice husk ash.

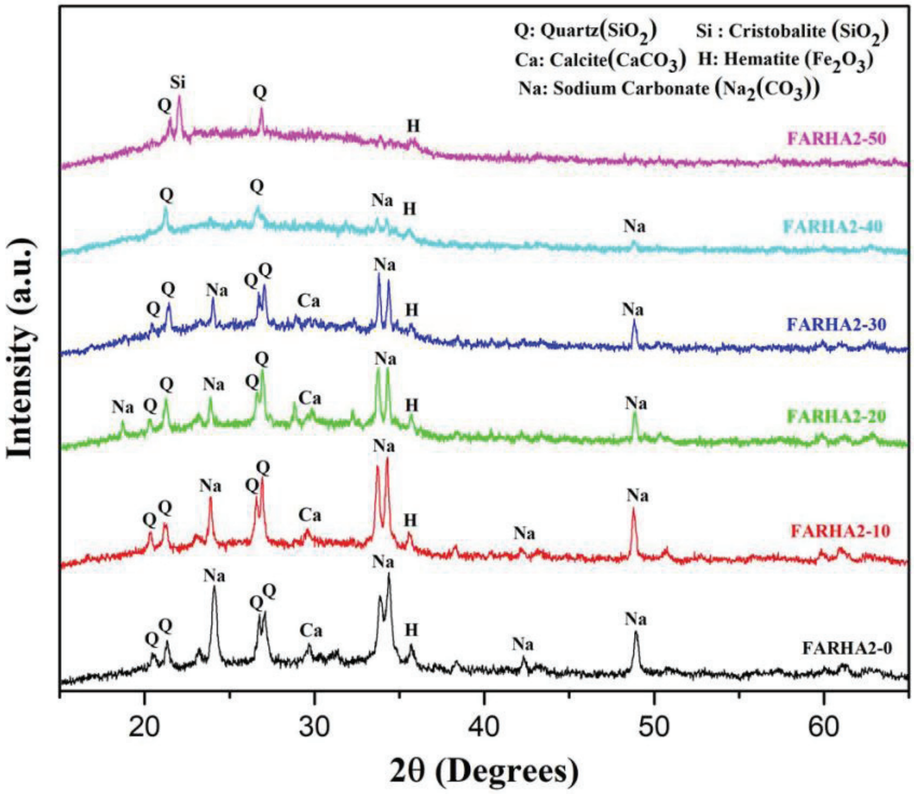

Figure 1. XRD pattern of porous geopolymer from fly ash and rice husk ash.

Microstructure figures show an increase in pore size through an increase in the rice husk ash ratio, as shown in Figure 2 These pores may be caused by the decomposition of polyester sponge (boiling temperature 350 °C) inside the workpieces attempt to exit. In addition, Detphan and Chindaprasirt (2009) reported that an increase in the rice husk ash ratio affected the rise of the SiO2/Al2O3 ratio which affected geopolymers with higher elasticity. The pressure from the enormous amount of gas pushes the pore wall to exit the structure. This phenomenon caused cracks in the FA, RHA-10, RHA-20, and RHA-30 but was not found in RHA-40 and RHA-50 specimens.

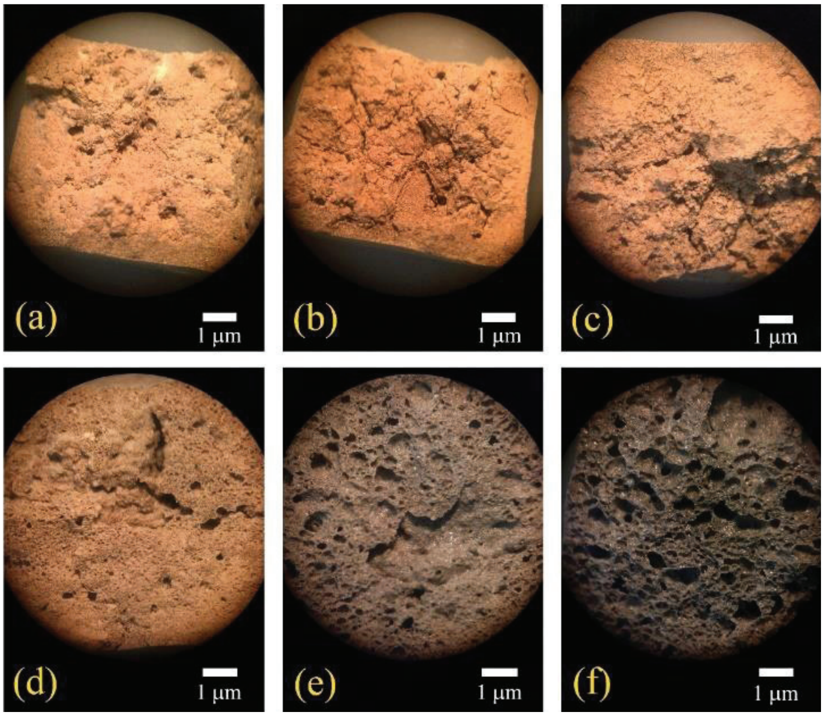

Figure 2. Cross section of the porous geopolymer using stereo camera at 10x (a) FA (b) RHA-10%, (c) RHA-20%, (d) RHA-30%, (e) RHA-40%, and (f) RHA-50%

In Figure 3, the percentage expansion increases due to an expansion of the geopolymer structure when the rice husk ash increase. This is likely caused by the water evaporation during the curing process attempt to escape from the structure, thus pushing the structure out (He *et al.*, 2013). This result corresponds to the pore size in the micrograph below.

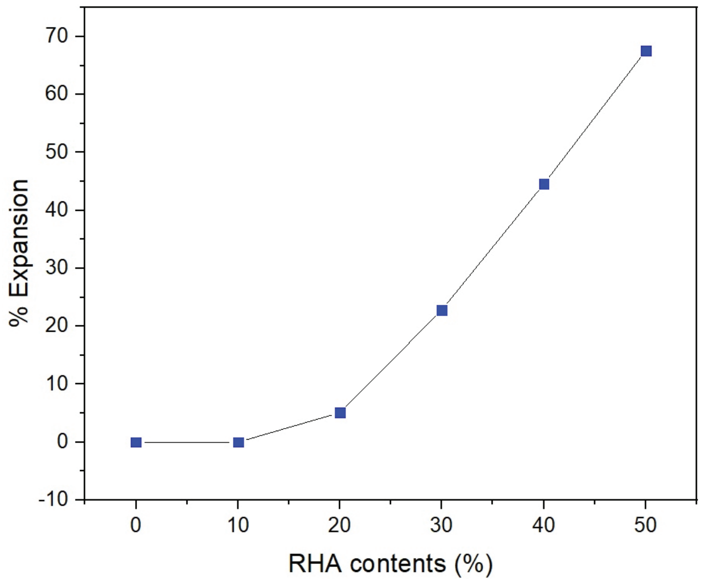

Figure 3. The % expansion of porous geopolymer from fly ash and rice husk ash.

The bulk density of the sintered geopolymer was determined via Archimedes principle. It was found that the bulk density decreased with the addition of the rice husk ash. The highest bulk density was found in 100% fly ash condition with 1.28 g/cm3, corresponding to Detphan and Chindaprasirt (2009). The gradually swelling of the prepared geopolymer is displayed in Figure 3 and Figure 4 with the increased content of RHA. This swelling is predictably related to the release of moisture and gas, which results from the dehydroxylation of hydroxides (Beaino, 2022). The water absorption and the apparent porosity of the prepared geopolymer are consistent with the percentage bulk density. From Figure 4, the water absorption and the apparent porosity are the highest value with 75% and 56%, respectively. The specimens from RH-40 and RH-50 cannot be observed according to their floating on water

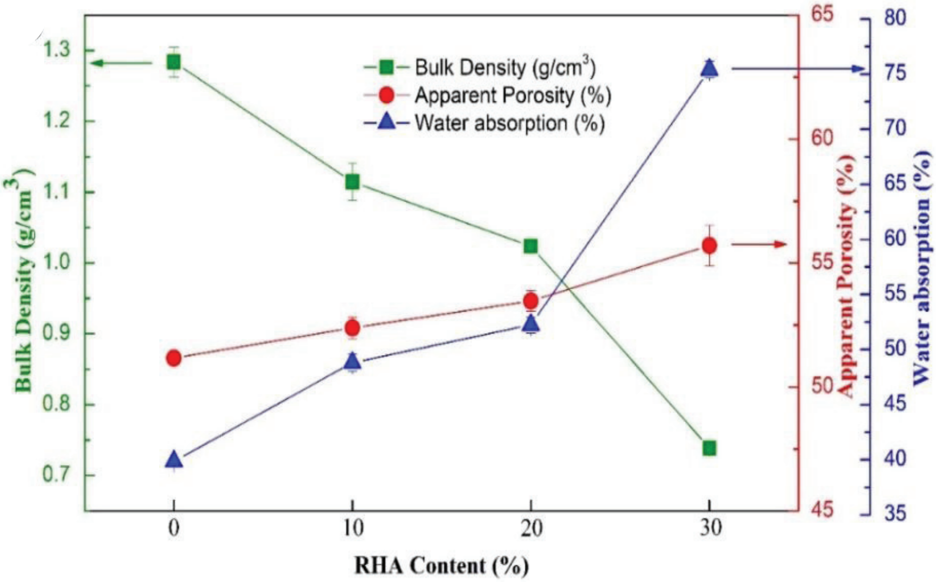

Figure 4. Bulk density, water absorption and apparent porosity of the prepared geopolymer.

4. Conclusion

An elevation in the rice hush ash ratio influences the depletion of calcite ($CaCO_3$) content in the studied geopolymer system. The silica and calcite ratio increment resulted which affected the expansion percentage reduction of the studied geopolymer structure. Moreover, the rising rice husk ash ratio affects the SiO_2/Al_2O_3 ratio addition, which affects the absence of cracks in the geopolymers due to their higher elasticity. Finally, the rice husk ash ratio influenced the physical properties of the geopolymer. All results present that the high rice husk ash ratio decreases the bulk density of the prepared geopolymer. The enormous pore in the studied geopolymer can increase water absorption and the apparent porosity.

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