EFFECT OF AGRICULTURAL WASTES WITH FLY ASH ON STRENGTH OF GEOPOLYMERS

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Abstracts

Cement is commonly used as the main material to produce concrete, however, the process of production of cement is causing environmental problems. The amount of CO_2 emission from cement industries due to the calcinations of limestone and combustion of fossil fuel is in the order of approximately one ton for every ton of cement produced. To produce environmentally friendly concrete called geopolymer, it was proposed that a new material could be produced by a polymerization reaction of alkali liquids with Si and Al as source materials of geological origin materials. Si and Al are derived from pozzolanic materials or aluminosilicate mineral powders, for example, powders of metakaolin or by-product of industrial and agricultural materials such as lignite ash and agricultural ashes. This research was conducted to study geopolymers made partly from < 45 μm powders of fly ash, bagasse ash and rice husk ash. Sodium hydroxide concentration of 10 molar (10MNaOH) and sodium silicate (Na_2SiO_3) solutions were used as alkali activators by the mass ratio of Na_2SiO_3:NaOH at 3:2. The geopolymer specimens were cured at room atmosphere for 7, 14, 21 and 91 days for characterization. SEM/EDS, XRF and UTM were carried out for microstructures, chemical compositions and compressive strength, respectively. Finally, the cost of production of specimens from cement and geopolymers were compared because of the the carbon tax concern

Keywords: Geopolymer, Fly ash, Bagasse ash, Rice husk ash, Compressive strength, Carbon tax

Introduction

The global cement industry produced around 3 billion tons of cement and emitted more than 2.4 billion tons of the carbon dioxide (CO_2) in 2009 (Carbon War Room, 2012) which was approximately 7% of the total man-made greenhouse gas emissions to the atmosphere. Therefore, it certainly causes global warming (Mehta, 2002). It is believed that one of the most challenging problems on the environment is caused by the construction industries focusing on cement production.

McCaffrey (2002) introduced three alternatives to reduce the amount of CO_2 emissions from the cement industries; namely,

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to decrease the amount of calcined materials in cement, to decrease the amount of cement in concrete and to decrease the quantity of cement using for buildings. Moreover, two stages of a short-term and a long-term process were proposed in the production of environmentally friendly concrete. A short-term effort was an attempt to use fewer natural resources with less energy and to decrease the CO_2 emissions, whereas the long-term view was to reduce the quantity of unwanted industrial by-products by lowering the rate of materials consumption (Mehta, 2002).

Geopolymer is one of alternatives to choose as a construction material. Hence, the use of geopolymer in order to replace the cement is to reduce the CO_2 emissions from the cement industries. Geopolymerization reaction can be applied to utilize solid wastes and by-products containing silica (SiO_2) and/or alumina (Al_2O_3) which are called pozzolanic materials or pozzolans. Pozzolans from industrial and agricultural wastes such as fly ash, bagasse ash and rice husk ash were handled to produce geopolymers in previous research (Tippayasam *et.al.*, 2010).

A waste with smooth, spherical and fine particles from power plants applied quite extensively as a pozzolan for geopolymers is fly ash for replacing cement. Bagasse is a waste from sugar refinery whereas rice husk is a waste from rice mill, and they are used as fuel to generate heat energy in their production processes. When they are burnt, both bagasse ash and rice husk ash contain more or less 80% of silica in which amorphous form was used as pozzolans Please add one. (Chindaprasirt *et.al.*, 2009).

The objectives of this research were to produce low cost and high strength geopolymer and to demonstrate the use of agricultural and industrial wastes in construction materials.

Materials and Method

Raw Materials Preparation

Fly ash (FA) was lignite fly ash from Mae Moh power plant in the northern part of Thailand. Bagasse ash (BA) was a waste from sugar refinery of Kaset Thai Co., Ltd., in Nakhon Sawan province, central Thailand. Rice husk ash (RHA) was obtained from rice mill in the central part of Thailand. FA, BA and RHA were ground by a centrifugal ball mill until whole of the fine particles passed through sieve No.325 mesh, i.e., < 45 µm particles were prepared as raw materials in the research.

Sodium silicate solutions (Na_2SiO_3) (13.8%Na_2O, 32.2%SiO_2 and 54.0%H_2O) and 10 molar sodium hydroxide solution (10M NaOH) (commercial grade) were used as the alkali activators.

Characterization of Initial Materials

FA, BA and RHA were determined by X-ray fluorescence (XRF), as shown in Table 1, to calculate the molar ratio of silicon to aluminum (Si/Al) and sodium to aluminum (Na/Al). The scanning electron microscope with energy dispersive spectrometer (SEM/EDS) was used to characterize the morphology of initial materials and resultant products, as shown in Figure 1.

Table 1. Chemical compositions of FA, BA and RHA determined by XRF (mass%)

Chemical composition (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
FA	39.88	22.36	13.22	12.85	2.56	1.72	3.09	2.97
BA	75.39	5.44	3.42	7.89	1.50	0.30	3.32	0.39
RHA	94.25	0.52	0.22	0.70	0.40	0.05	2.26	0.82

Mixed Proportions of Geopolymer Paste

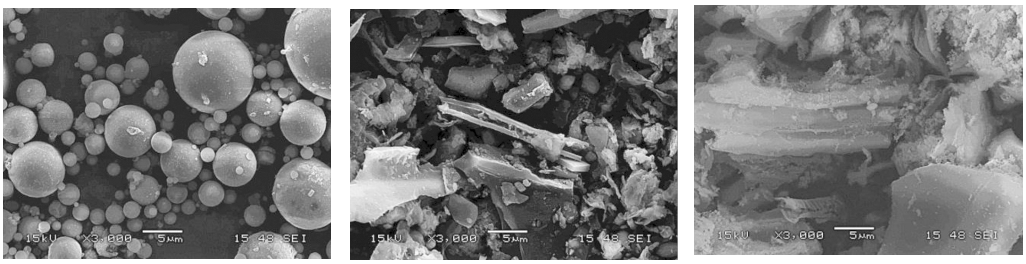
Geopolymer pastes were prepared from FA, BA and RHA as pozzolans in the alkali activators. The alkali activators or liquid was obtained from sodium silicate solution (Na_2SiO_3) and 10 molar sodium hydroxide solution (10M NaOH) with molar ratio of Na_2SiO_3:10M NaOH was 3:2 prepared at least 1 day prior to the experiments. The experimental ratios of pozzolan solid to alkali liquid were 80:20, 70:30, 60:40 and 50:50 by weight as geopolymer pastes. The calculation of the Si/Al and Na/Al molar ratios where initiated with the mixture of each pozzolan. However, the limitation of Si/Al molar ratio was found in case of BA and RHA possessing very high SiO_2 but very low Al_2O_3, in Table 1. Therefore, FA was brought in to compensate for expected Si/Al molar ratio.

For preliminary compressive strength test of geopolymer specimens in the research at 7 days, it was found that the optimum quantity of alkali liquid in terms of good flowability was summarized as 1) 20% alkali liquid for single FA geopolymer, 2) 50% alkali liquid for single BA or RHA geopolymers, and 3) 40% alkali liquid for blended FA with BA or with RHA geopolymers. Then, the mixtures of FA/BA and FA/RHA follow in Table 2 were mixed individually in a beaker. After that, the geopolymer pastes with suitable ratio of blended pozzolan solid to alkali liquid 60:40 by weight were prepared. The alkali solution was poured into a mixer and mixed with pozzolan mixtures homogeneously. Consequently, the pastes were poured into a 25 × 25 × 25 mm^3 acrylic mold. The molds were placed in tight-fitting lid containers to prevent specimens from oxidation with air and then cured at room temperature for 3 days. After demolding, the specimens were prevented from air and cured at room temperature until 7 day age. A scanning electron microscope (SEM) for microstructure analysis and a universal testing machine (UTM) for compressive strength test were employed. The compressive strength of geopolymer cubes was investigated according to ASTM C 109. Finally, 1 kg of cement and the geopolymer mortar production costs were calculated and compared due to carbon tax concern (The EU ETS, 2012).

Results and Discussion

Compressive Strength

Geopolymer pastes of FA-based were mixed more easily than those of other pozzolans, and used low quantity of alkali liquid to synthesize for high strength geopolymers (Figure 2). The reason for easy processing was probably because of the morphology of FA (Figure 1a) which is spherical shape and distributed size. The FA100L20 (100% fly ash and 20% alkali liquid) specimens presented high compressive



(a) (b) (c)

Figure 1. Microstructures of initial ashes, (a) FA: smooth and spherical shaped (b) BA fine, long and irregular shaped and (c) RHA: coarse, agglomerated and irregular shaped, 3000X

strength (24.7 MPa). In addition, it was found that the compressive strength of FA-based geopolymers obviously dropped when the percentage of alkali liquid exceeded 30%.

Compressive strength of specimens of BA and RHA-based geopolymers was found to be lower than that of FA-based. Their compressive strength trend increased as the quantity of alkali liquid increased to 50%. Alkali liquid was consumed more by geopolymers of BA and RHA-based than by those of FA-based because BA and RHA are hydrophilic (Phrommedetch, 2010). However, 40% alkali liquid was considered being more suitable because of higher stability when specimens of 40% and 50% alkali liquid were tested for leaching. It was concluded that the 100% BA and 100% RHA with both 40% and 50% alkali liquid were inappropriate to produce geopolymers due to their low compressive strength results. The reasons for low strength probably arose from the high Si/Al molar ratio because of the percentages of very high SiO_2 (75.39 and 94.25) but very low Al_2O_3 (5.44 and 0.52) contents of BA and RHA, respectively. Therefore, we thougth to blend BA and RHA with other pozzolan which possessed less Si and higher Al in order to compensate and control the Si/Al molar ratio to be 2 to 3. In this case, the pozzolan introduced to adjust for the expected molar ratio by lowering SiO_2 and adding up Al_23

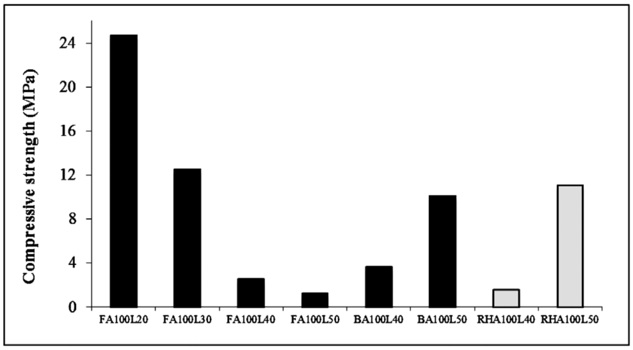


Figure 2. The compressive strength of 100% FA, BA and RHA geopolymers at 7 days

Table 2. Si/Al molar ratios and Na/Al molar ratios at 40% alkali liquid

Formulae	Si/Al molar ratio	Na/Al molar ratio
FA100	1.7	0.3
BA100	177.9	32.3
RHA100	13.9	3.1
FA90BA10	2.1	0.5
FA80BA20	2.5	0.5
FA70BA30	2.9	0.6
FA90RHA10	2.3	0.5
FA80RHA20	2.8	0.6
FA70RHA30	3.5	0.6

content in the system was FA, 39.88% SiO_2 and 22.36% Al_2O_3.

Therefore, FA was chosen to be blended with BA and RHA in order to promote compressive strength of geopolymers prepared from agricultural wastes. It was found that the geopolymers synthesized from FA mixed with either BA (FA/BA geopolymers) or RHA (FA/RHA geopolmers) were stronger than those from single ashes. At an early age from 7 to 21 days, the compressive strength of geopolymers of FA/BA presented the superior results, however, those of FA/RHA developed higher strength with longer curing time (21-91 days). The Si/Al molar ratio, amount of alkali liquid, types of pozzolans and Na/Al molar ratio were considered.

Microstructures of Geopolymer

The fracture surface of the geopolymer specimens were characterized by SEM, shown in Figure 4. It was found that spherical particles of FA embedded and joined in matrix with BA (Figure 4a) better than with RHA (Figure 4b). It have been observed that plenty of cracks originated in matrix with RHA more than with BA obviously, and this cracks occurred possibly from particles of RHA which were bigger than those of BA. Probably, much finer than 45 µm particles of BA and RHA would be introduced to the experiment to secure the reaction of polymerization and to promote the strength of geopolymers.

The appearance of cluster of white crystals on surface of specimen of FA70BA30 with 40% alkali liquid in Figure 5, determined by SEM/EDS, was Na and O. It was believed that white crystals were probably Na_2O crystals which arose from Na^+ in solution reacting with O_2 in the air. Therefore, it was

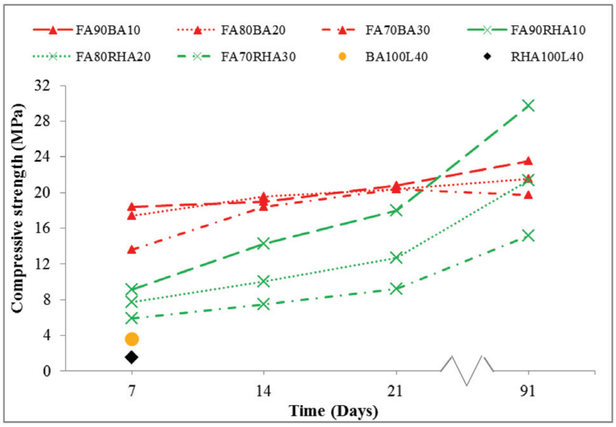
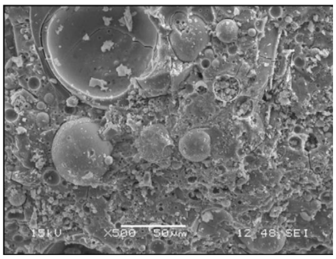
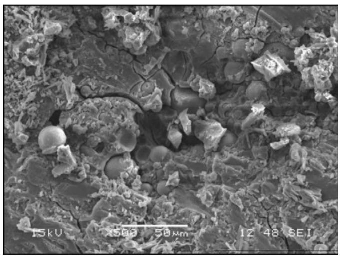


Figure 3. The compressive strength of geopolymer specimens with 40% alkali liquid at 7, 14, 21and 91 days



(a)



(b)

Figure 4. Fractural microstructure of geopolymers of (a) FA + BA and (B) FA + RHA at 21 days

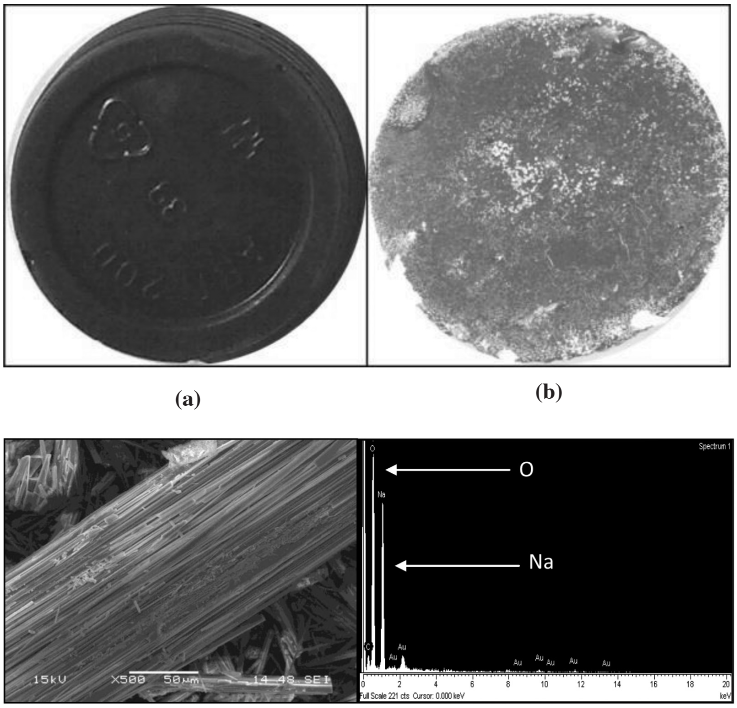


Figure 5. **(a) specimen of FA70BA30 with 40% alkali liquid in tight-fitting lid container for 7 day (b) specimen of FA70BA30 with 40% alkali liquid in air for 7 day (c) and (d) Microstructures with chemical composition of white crystals on surface of specimens characterized by SEM/EDS, 15kV, 500X**

Table 3. **The production cost of cement mortar and FA90RHA10 geopolymer mortar**

Initial materials	**Price (US $)**	**Cement**		**Geopolymer**	
		Amount (kg)	**Price (US $)**	**Amount (kg)**	**Price (US $)**
Portland cement	0.12	0.18	0.02	-	-
Water	0.01	0.32	0.003	0.18	0.002
Sand	0.05	0.50	0.03	-	-
Fly ash	0.03	-	-	0.54	0.02
Bagasse ash	0.00	-	-	0.06	0.00
10 M Sodium hydroxide	2.67	-	-	0.08	0.21
Sodium silicate	2.00	-	-	0.14	0.28
Carbon tax	0.05	0.18	0.01	-	-
Total	**1.00**	**0.06**	**1**	**0.51**	

Remark: Carbon tax would be 50 US dollars per tons of carbon dioxide (CO2): The EU ETS suggested that specimens of geopolymers should avoid oxidation at the beginning of geopolymerization reaction by tight-fitting lid containers, otherwise, the compressive strength would not be satisfactory because Na^+ would not mainly be brought to react in geopolymerization but to react with O_2 forming as sodium oxide instead.

The Cost of Cement Mortar Compared with Geopolymer

FA90RHA10 with 40% alkali liquid was chosen to calculate for cost of geopolymer mortar calculation because it gave a good compressive strength at old age and consumed the RHA up to 10%. From Table 3, it was calculated from the ratio of cement: water = 1: 0.48 for cement mortar and the weight ratio of pozzolans: alkali liquid = 0.6: 0.4 for geopolymer mortar. Carbon tax from cement industry was used to calculate the cost of cement mortar. The cost of 1 kg mortar production from both cement and geopolymers was compared and it was concluded that geopolymer was a little more expensive than cement for approximately 0.45 US dollar/kg. However, geopolymers are is an alternative construction material for the future in terms of environment concerng to reduce CO_2 emission.

Conclusion

Pozzolans used in the research were < 45 μm FA, BA and RHA. Compressive strength of geopolymers of FA with either BA or RHA was higher than that of single BA or RHA BA or RHA. The FA/BA geopolymer presented good strength at early age while the FA/RHA developed its strength at older age. The proper alkali liquid of blended FA/BA and FA/RHA was 40% by weight. Finally, cost of mortar production from geopolymers was a little more expensive than that from cement for approximately 0.45 US dollar/kg.

Acknowledgements

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References

Carbon War Room. (2012). The Cement, Washington, D.C.: Carbon War Room. Available from: www.carbonwarroom.com. Accessed date: August 10, 2012.

Chindaprasirt, P., Sirivivatnanon, S., and Rukzon, V. (2008). Resistance to chloride penetration of blended Portland cement mortar containing palm oil fuel ash, rice husk ash and fly ash. Construction and Building Materials. 22: 932-938.

McCaffrey, R. (2002). Climate Change and the Cement Industry, Global Cement and Lime Magazine (Environmental Special Issue):15-19.

Mehta, P.K., (2002). Greening of the Concrete Industry for Sustainable Development, ACI Concrete International, 24(7): 23-28.

Phrommedetch, S. (2010). Compatibility Improvement of Rice Husk and Bagasse Ashes with Natural Rubber by Molten-State Maleation. European Journal of Scientific Research. 43: 411-416

The European Emissions Trading System [EU ETS]. (2012). Carbon tax. Brussels: EU ETS. Available from: www.ec.europa.eu. Accessed date: August 12, 2012.

Tippayasam, C., Boonsalee, S., Sajjavanich, S., Ponzoni, C., Kamseu, E., and Chaysuwan, D. (2010). Geopolymer Development by Powders of Metakaolin and Wastes in Thailand. Advances in Science and Technology. 69: 63-68.