PREPARATION OF GEOPOLYMER USING FLY ASH AND RICE HUSK SILICA AS RAW MATERIALS

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Abstract: Fly ash was used as raw material for making geopolymer. The samples were prepared by mixing fly ash and activator: sodium hydroxide (NaOH) with varying the proportion of H_2O and Na_2O. In addition, the possibility of using rice husk ash (RHA) as a partial replacement for fly ash raw material was studied. After mixing, the mixtures were casted in a plastic mold and left to harden for 48 hr at room temperature and 60°C and further cured for 7 days. The existing phases were investigated by using XRD. Bending strength and density of the geopolymers were also examined. Results showed that the amount of H_2O and Na_2O in the mixtures had an effect on the properties of geopolymer. The strength decreased with an increase in H_2O mol ratio and the appropriate mol ratio of Na_2O was 1.0. The addition of RHA as a silica source also had an effect on the strength of geopolymer. The strength increased with an increase in silica content.

1 Introduction

Geopolymer is an amorphous alumino-silicate material. Its structure is silicon and aluminium atoms bonding together by sharing oxygen atoms. Once the alumino-silicate powder was mixed with alkaline solution, a paste formed and transformed to hard material and gained strength [1]. Geopolymer was applied in many fields such as a replacement of Portland cement because its production lower energy and does not release the green house gases and use in building and mortar applications because of their short time strength development [2-4]. Geopolymer was prepared by dissolution of raw materials which have silica and alumina such as metakaolin and fly ash in alkaline solution [5].

In this study, geopolymer were prepared by using fly ash from power plant in Thailand as a raw material and the proportion of H_2O and Na_2O was varied to study their effect. Furthermore, the use of rice husk ash (RHA), by product from agriculture was studied to test possibility for apply as a replacement of fly ash

2 Experimental procedures

2.1 Raw materials and mixture compositions

Fly ash, rice husk ash and sodium hydroxide (NaOH) were used as raw materials. The fly ash used was supplied by Mae Moh power plant in Lampang, Thailand. Its chemical analysis demonstrated that the fly ash was composed of SiO_2, Al_2O_3, Fe_2O_3 and CaO as the major component [5, 6]. Rice husk ash was obtained by burning the rice husk at 600°C for 2h in an electric furnace. The obtained rice husk ash was amorphous phase which was confirmed by XRD.

Two series of mixtures were used in this experiment. In the first series, the mixtures was prepared by mixing fly ash and NaOH with varying the H_2O and Na_2O mol ratio in order to investigate the effect of H_2O and Na_2O on the properties of geopolymer. The compositions of the mixtures in this series are shown in *Table1*. For the second series, some amount of fly ash was replaced by rice husk ash. The amount of rice husk ash silica was varied from 5-15 wt% as the compositions shown in *Table2*.

Table1. Mixture compositions of sample in 1st series

Formula	Mol ratio			
	SiO_2	Al_2O_3	Na_2O	H_2O
9.0H-1.0N	3.29	0.89	1.0	9.0
11.0H-0.5N	3.29	0.89	0.5	11.0
11.0H-1.0N	3.29	0.89	1.0	11.0
11.0H-1.5N	3.29	0.89	1.5	11.0
13.0H-1.0N	3.29	0.89	1.0	13.0
15.0H-1.0N	3.29	0.89	1.0	15.0
17.0H-1.0N	3.29	0.89	1.0	17.0
19.0H-1.0N	3.29	0.89	1.0	19.0
23.0H-1.0N	3.29	0.89	1.0	23.0

Table2. Mixtures composition of sample in 2nd series

Formula	Mol ratio			
	SiO_2	Al_2O_3	Na_2O	H_2O
100FA-0RHA	3.29	0.89	1.0	11.0
95FA-5RHA	3.34	0.79	1.0	11.0
90FA-10RHA	3.61	0.75	1.0	11.0
85FA-15RHA	3.87	0.71	1.0	11.0

2.2 Preparation of geopolymer specimens

Firstly, sodium hydroxide (NaOH) was dissolved in distilled water. Then weighted quantities of raw materials: fly ash and rice husk ash were added into the NaOH solution and mixed until the mixtures looks homogeneous. The mixtures were cast in a plastic mold and cured at two temperatures (room temperature and 60°C) for 48 hours. After that, the specimens were cured continuously at room temperature for 7 days.

2.3 Characterization of specimens

The geopolymer specimens were characterized by bending strength, X- ray Diffraction (XRD) and density.

After aging at room temperature for 7 days, the geopolymer specimens were tested for bending strength by using testing machine HT-8116. The size of tested samples was 18x12x90 mm and the span length was 80 mm. Values were the averages of three samples with error reported as average from mean.

The specimens were ground and passed through a 325 mesh screen to obtain the powder for phase analysis. The phase analysis was determined by using X-ray Diffractometer (XRD), Bruker D8 Advanced machine with the scanning angle of 10-70 degree.

Bulk density was measured according to ASTM-C 830-00 [7]. Density values were the averages of five samples and error reported as average from mean.

3 Results

3.1 Effect of mol ratio of H_2O and Na_2O

The viscosity of the mixture with low mol ratio of H_2O (9.0 mol) was so high that it was difficult to pour into the plastic mold. This suggests that this proportion of H_2O is not suitable for utilization.

The bending strength plotted in *Fig. 1* was the average number of three specimens. After cured at 60°C, the bending strength of some specimens could not be measured because the cracks were observed on their surface. It can be seen from *Fig. 1* that bending strength of specimens decreased with an increasing in water ratio.

The strength of geopolymer increases with decreasing water ratio in alkaline solution. Due to during mixing, Ca^{2+} ion from fly ash reacts with OH^- in alkaline aqueous solution and forms $Ca(OH_2)$. Then $Ca(OH_2)$ reacts with CO_2 in atmosphere to form calcite ($CaCO_3$) [1].

From this study, the H_2O ratio which provided optimum rheology and strength was 11.0 mol.

Bulk density of specimen is shown in *Fig.2*. It deceased with increasing the amount of H_2O. Apparent densities of these specimens were 2.34-2.43 g/cm^3. Water absorption was range from 26.48-56.64%. The porosity is thought to be mostly open pores. Comparing with *Fig.1*, the bulk density had the same trend as the bending strength.

The optimum amount of Na_2O ratio was 1.0 as shown in *Fig.3*. *De Silva and Sagoe-Crenstil (2008)* prepared geopolymer from metakaolinite. They found that when Na_2O ratio increased, the strength decreased [8]. *S. Songpiriyakij et al. (2010)* prepared geopolymer from fly ash and rice husk and bark ash and found that with decreased in Na_2O ratio the strength of geopolymer increased [2]. High Na_2O content affected to amorphous-crystalline transformation in the system. The higher strength was achieved if the amorphous matrix was dense [5, 8].

The optimum mol ratio was 3.29SiO_2, 0.89Al_2O_3, 11.0H_2O and 1.0Na_2O and this formula was used in the second series of the experiment.

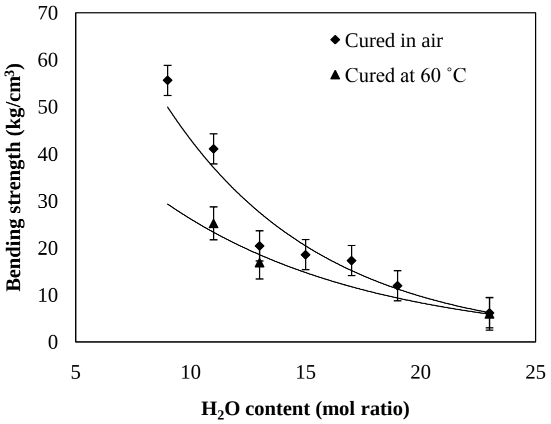

Fig.1 Bending strength of specimens as a function of H_2O mole ratio

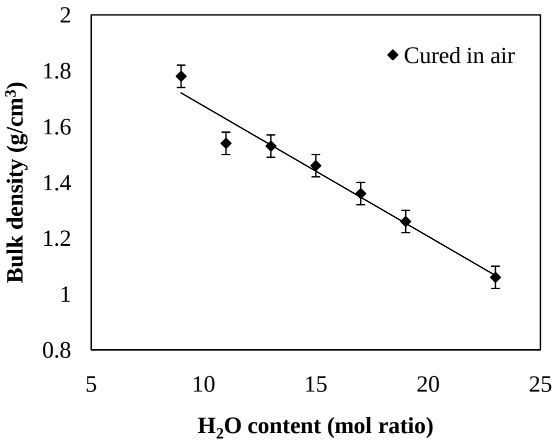

Fig.2 Bulk density as a function of H_2O mole ratio

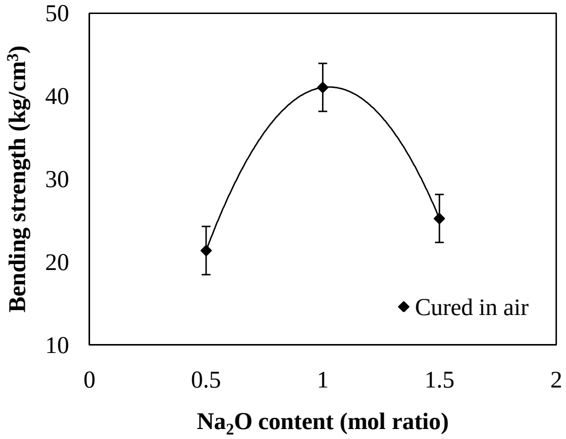

Fig.3 Bending strength of specimens as a function of Na_2O mole ratio

3.2 Effect of RHA

When fly ash was replaced by RHA, the bending strength increased dramatically as shown in *Fig.4*. The SiO_2/Na_2O ratio affects to degree of polymerization of dissolved ions [1, 9]. *Provis and Van Deventer (2007)*, state that when silica content increases, the rate of the reaction occurs in geopolymer paste decreases. The solidification of the paste may be completely reaction [1, 10, 11]. With increasing of RHA content, SiO_2 increases. So the SiO_2/Al_2O_3 ratio also increases. The product which has high SiO_2/Al_2O_3 ratio provides higher strength [1, 12]. *Fletcher et al. (2005)* synthesized geopolymer from dehydroxylated kaolinite and amorphous silica. They found that high Al_2O_3 compositions provided low strength [1, 13]. *De Silva and Sagoe-Crenstil (2008)* found that in the increasing of SiO_2 ratio the strength also increases [8]. *S. Songpiriyakij et al. (2010)* found that the strength increased with the increasing of SiO_2/Al_2O_3 ratio. When rice husk and bark ash was added, the strength increased. Rice husk and bark ash provided Si in the mixture and formed stronger Si-O-Si bonds [2].

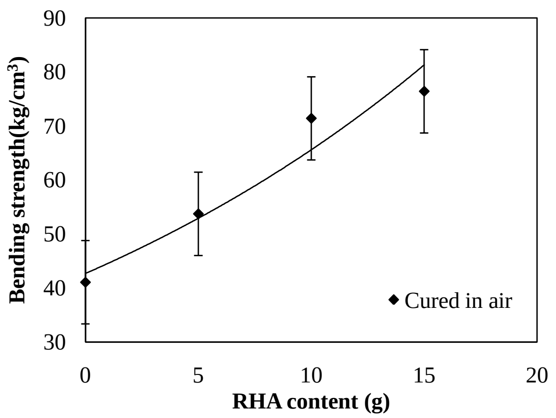

Fig.4 The relationship between bending strength and RHA content.

3.3 X- ray Diffraction (XRD) results

From XRD pattern, all of samples in first part of the experiment had similar phases as same as fly ash, it was the result from an incomplete reaction between raw materials. The major phases of these geopolymer are calcite($CaCO_3$) and calcium silicate(Ca_3SiO_5) as shown in *Fig.5*. It indicated that the H_2O content does not affect to appearance phases. However, the intensity of peak of each formula is not so similar. When the amount H_2O increased the peak intensity decreased. It means that the crystal phases in specimen decreased and the broad band peaks around 28 degree (2θ) which corresponding to geopolymer peak were slightly increased [8].

X. Guo et al (2010) synthesized geopolymer from fly ash and XRD pattern was observed. The large part of the structure was amorphous. However the crystalline phases also generated, quartz, Gismondine(zeolite) and calcium silicate hydrate. Peaks of quartz resulted from unreacted fly ash [4].

E.I. Diaz et al (2010) synthesized geopolymer from fly ash with different calcium content. The XRD pattern also showed that there are amorphous and crystalline phases. The crystalline phases still remain after the reaction of fly ash, quartz, mullite, merwinite and calcite [14].

U. Rattanasak, and P. Chindaprasirt (2009) studied on leaching of fly ash mixed with NaOH solution and on mixing procedure for preparing geopolymer. From XRD pattern, the geopolymer consisted of amorphous alumino-silicate phase which similar to crystal of quartz and mullite from fly ash which was raw materials [15].

It indicated that the existing phases of geopolymer are amorphous phase and the crystalline phases. Some crystalline phases came from unactivated raw materials.

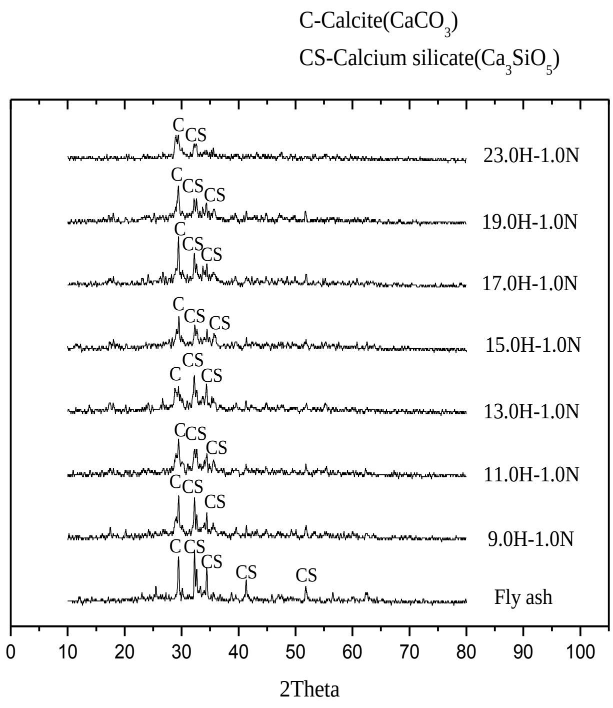

Fig.5 XRD of samples with varied H_2O mole ratio.

For XRD pattern of geopolymer samples which Na_2O content was varied (*Fig. 6*), these samples also had similar existing phases as fly ash. The intensity of calcite and calcium silicate peaks decreased with increasing in Na_2O mole ratio. Therefore, the Na_2O content affects the dissolving of phases in fly ash.

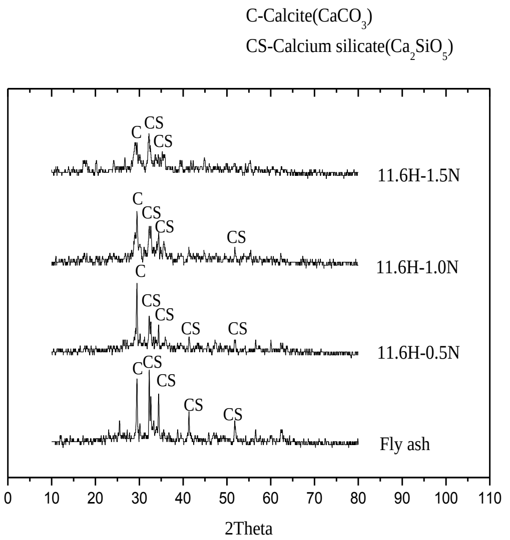

Fig.6 XRD of samples with varied Na_2O content

For the specimens with RHA, the major phases of sample in this part are calcite($CaCO_3$), calcium silicate (Ca_3SiO_5) and quartz(SiO_2). Quartz appeared in samples which had 10g and 15g of RHA. Increasing the amount of RHA, $CaCO_3$ and Ca_3SiO_5 decreased while amorphous phase slightly increased as shown in *Fig 7*.

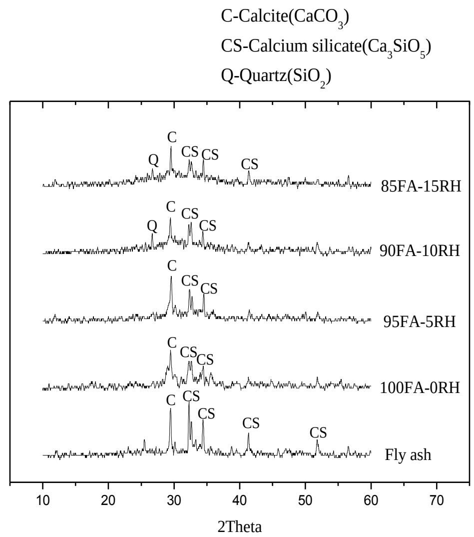

Fig.7. XRD of samples with varied RHA amount

4 Conclusion

The results of this study can be summarized as follows:

- The mol ratio of both H_2O and Na_2O had the effect on the properties of geopolymer.

- The bending strength and density of geopolymers decreased with increasing in the mol ratio of H_2O.

- The appropriate mol ratio of Na_2O was 1.0

- Calcite ($CaCO_3$) and calcium silicate (Ca_3SiO_5) was found as the major phases in the geopolymers.

- Rice husk ash can be used as a silica source partially replace for fly ash. And the bending strength of geopolymer increased when the amount of rice husk ash increased.

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