INVESTIGATION ON WATER ABSORPTION CAPABILITY FOR DIFFERENT MOLARITY OF RICE HUSK ASH BASED POZZOLAN BINDER

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Abstract

Presence of more than 80% of silica and 3% of alumina makes rice husk ash as potential materials for producing geopolymer. Combination between super pozzolanic bio-waste materials such as rice husk ash with different molarity of alkaline activated solution expected to produce geopolymer materials with difference water absorption properties. In this paper, molarity of sodium hydroxide (NaOH) solutions are varied from 4 to 16M and the solid to liquid ratio are varied from 1.0 to 1.5 for each molar. Water absorption for any geopolymer in this work was found to decrease with increasing the concentration of NaOH. Presence of cracks on the geopolymer structure as seen from micrograph image under Scanning Electron Microscope (SEM) shows the effect of water absorption in geopolymer, where sample S05 with 4M of NaOH is the only sample that showed the structure still remains intact and has less degradation. However, decrease in water uptake after 20 days was attributed to the improvement on the microstructure of the geopolymer.

Keywords: Alkaline activator solution, Geopolymer, Pozzolan, Rice husk ash, Water absorption.
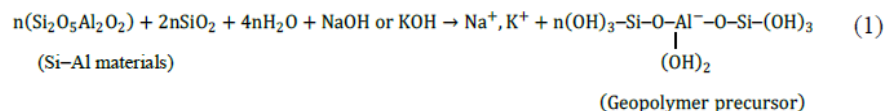
1. Introduction

Future aircraft demands the use of green materials due to its renewable resource and concern for the environment. Currently, most of the polymer resins which are used in making composite or as parts and components such as epoxy are largely derived from petroleum. Developing an alternative materials for interior part of aircraft from renewable resource can potentially reduce the dependant on the petroleum source. One of the alternative materials which is possibly to be use is geopolymer. Geopolymer was invented by Davidovits in 1978 to represent a broad range of materials characterized by chains or networks of inorganic molecules [1] and the term geopolymer seldom used in both academically and commerciality in terms of marketing rather than scientific purposes [2].
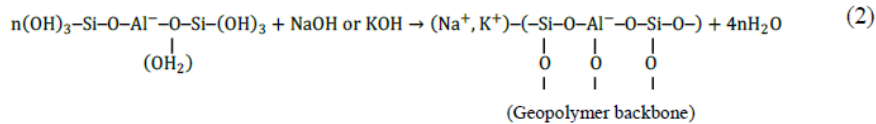
Geopolymer binder also known as part of innovative technology that is generating considerable interest in the construction industry, particularly in light of the ongoing emphasis on sustainability. Interestingly, it is high temperature resistance, lightweight and fire proof properties up to over $1000^{\circ}C$ with long term exposure makes geopolymer as choice of materials for automotive and aerospace industries. The sources of geopolymer materials dependant on thermally activated natural materials (e.g., kaolinite clay), industrial by-products (e.g., fly ash or slag) and agricultural waste (e.g., rice husk ash, palm oil fuel ash, bagasse ash). Incorporation of pozzolanic waste in producing geopolymer could promote energy saving by recycling the ash waste materials. Subsequently, reduce the environmental pollution due to the massive solid pozzolanic waste disposal that occupied vast field.

Geopolymer produced with fly ash have been used widely as the most well stable geopolymer among others inorganic products and fly ash was the first used in concrete in the USA since 1930s [2]. While rice husk ash have been studied extensively by most researchers in making geopolymer due to its high silica content. On top of that, every year more than 700 million tonnes of rice is harvested worldwide and 22% of husk is produced from paddy milled. During firing process, 25% of the rice husk turn into rice husk ash. Chemical reaction between aluminosilicates oxides from rice husk ash and alkaline solution yield formation of amorphous or semi-crystalline polymeric structures of Si-O-Al bonds.

Another important factor that affects the properties of geopolymer is the size and shape of the pozzolanic precursors [3]. Moreover, presence of water, oxygen and carbon dioxide tends to affects the durability of geopolymer materials [4]. Presence of water through the pore channel in geopolymer structure can cause its deterioration. In addition, water absorption in geopolymer can be dependent on the pore diameter, pore distribution, continuity and tortuosity [5].

Pozzolanic materials sources provide high amount of silicon and aluminium element which is soluble in an alkaline activating solution and subsequently polymerizes the pozzolanic materials into molecular chains and networks to create the hardened binder called geopolymer. Chemically, geopolymer can be produce in the form of -Si-O-Al-O- or -Si-O-Al-O-Si-O- or -Si-O-Al-O-Si-O-Si-O- and the schematic arrangement on the formation of geopolymer material can be described as follow [6]:

$$n(Si_2O_5Al_2O_2) + 2nSiO_2 + 4nH_2O + NaOH \text{ or } KOH \rightarrow Na^+, K^+ + n(OH)_3-Si-O-Al^--O-Si-(OH)_3 \quad (1)$$

$$\text{(Si-Al materials)} \qquad \qquad \underset{|}{\overset{|}{(OH)_2}}$$

$$\text{(Geopolymer precursor)}$$

$$n(OH)_3-Si-O-Al^--O-Si-(OH)_3 + NaOH \text{ or } KOH \rightarrow (Na^+, K^+)-(-Si-O-Al^--O-Si-O-) + 4nH_2O \quad (2)$$

$$(OH_2) \qquad\qquad\qquad\qquad\qquad\quad O \quad O \quad O$$

$$\text{(Geopolymer backbone)}$$

Equation (2) showed water released during the fabrication process of geopolymer. According to Aliabdo et al. [6], the water is removed from geopolymer matrix along the curing and drying process which then leave formation of nanopores in the geopolymer structure. Therefore, presence of water during geopolymerization process was to provide ease of workability during mixing process and it does not relate to the chemical reaction interaction [7]. On the other hand, increasing the geopolymeric reaction tends to improve the strength of the geopolymer structure and reduce the water absorption inside the geopolymer structure as well [8]. According to the Nazari and Sanjayan [8], there are two phenomena related to high water absorptions. First, it can be related to incomplete reactions of the geopolymer mixtures and second is due to the porosity nature of geopolymer which increase the tendency in absorbing water.

This research study was intended to explore the feasibility of water absorption of geopolymer based on rice husk ash (RHA) produced with different molarity of alkaline activators. Water absorption effects on the geopolymer samples have been conducted for 50 days and the morphology on the geopolymer structure after water absorption test was observed under Scanning Electron Microscope (SEM).

2. Materials and Methods

2.1. Preparation and characterization of RHA

Rice husk ash (RHA) were obtained from Maerotech Sdn Bhd. The RHA was initially grinded into finer particles using planetary mill Pulverisette 4. The ground RHA was sieved and particle size distribution (PSD) test was conducted on the RHA sample. The particle size of RHA was found to be in the range from 3.4 to 59.5μm and its specific area was 0.701m^2/g. The chemical composition of the RHA is determined using XRF and are shown in Table 1. SiO_2 was found to be the major constituent in RHA which is about 87%.

Table 1. Chemical composition of rice husk ashes.

Compound	Concentration Unit %	Compound	Concentration Unit %
Al_2O_3	3.0	Fe_2O_3	1.49
SiO_2	87.4	NiO	0.068
K_2O	0.49	CuO	0.045
CaO	1.4	ZnO	0.035
Cr_2O_3	0.27	PdO	6.0
MnO	0.19		

Sodium silicate (Na_2SiO_3) comprise of H_2O = 30.3%, Na_2O = 11.9% and SiO_2 = 57.8%. Sodium hydroxide (NaOH) is prepared with different molarity starting from 4M, 8M, 12M, and 16M. The NaOH solution was prepared by dissolving the NaOH solution in distilled water.

2.2. Mixing process

Initially, alkaline activator consisted of different molarity of NaOH and Na_2SiO_3 were prepared and denoted as alkaline activator (AA) solution. The RHA was then combined with AA to form geopolymer solution by stir gently for 30 seconds followed by stirring using mechanical stirrer for another 30 minutes until the solution become homogeneous. The mixture was then cast onto a mold size 70 mm × 50 mm × 12 mm. The geopolymer samples was then cured for 24 hours at 75 ⁰C in oven. Table 2 shows the mixture proportion for each geopolymer sample produced.

Table 2. Mixture proportion for geopolymer samples.

Sample	Ratio RHA to AA	Ratio Na_2SiO_3 to NaOH	NaOH Molarity	Sample	Ratio RHA to AA	Ratio Na_2SiO_3 to NaOH	NaOH Molarity
S01	0.5	0.5		S13	0.5	0.5	
S02	0.5	2.5		S14	0.5	2.5	
S03	1.0	0.5	4	S15	1.0	0.5	12
S04	1.0	2.5		S16	1.0	2.5	
S05	1.5	0.5		S17	1.5	0.5	
S06	1.5	2.5		S18	1.5	2.5	
S07	0.5	0.5		S19	0.5	0.5	
S08	0.5	2.5		S20	0.5	2.5	
S09	1.0	0.5	8	S21	1.0	0.5	16
S10	1.0	2.5		S22	1.0	2.5	
S11	1.5	0.5		S23	1.5	0.5	
S12	1.5	2.5		S24	1.5	2.5	

2.3. Water absorption test

The water absorption test in this research is followed the standard of ASTM D570. The geopolymer samples that used for water absorption test were immersed in a water bath at room temperature for some period of time until they reach equilibrium. However, at some intervals, the samples are taken out for weighing procedure and re-immersed into water again. The percentage of the water content (M_t) was determined using Eq. (3) [7]

$$M_t(\%) = (\frac{W_t - W_o}{W_o}) \times 100 \tag{3}$$

where W_t is the weight of the sample at time t and W_o is the initial weight of the sample.

2.4. Microstructural analysis

The microstructure of the geopolymer were examined using Hitachi S-3400N SEM. The test concentrates on the interface between the particles of the rice husk ash and the alkali activator after the water absorption test. The samples are prepared by cutting into small pieces and coated with a thin layer of gold.

3. Results and Discussions

3.1. Water absorption

The effect of water absorption on the geopolymer samples produced with different NaOH concentration is highlight in Fig. 1. From this figure, there are four graph

(a-d) with different NaOH concentration showed the trend of water absorption for different sample composition on each concentration. Figure 1(a) shows that the geopolymer sample produced with 4M NaOH concentration initially increase in weight gain in the range of 5 to 10 days of soaking. Apparently, sample S04 shows the highest weight gain among all samples in this concentration. Then, for sample produce using 8M of NaOH concentration, only two sample absorb high amount of water, while the rest of the sample has lost its intact structure and the geopolymer start to dissolve due to high amount of water absorption.
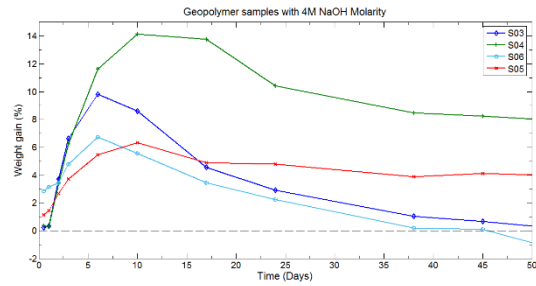
Samples in Fig. 1(c) shows that sample S15 absorb high amount of water, while sample S18 water absorption start to decrease after 15 days. In addition, samples in Fig. 1(d) shows that sample S21 absorb the highest amount of water compared to other sample produced using 16M NaOH. Thus, it is expected that some portion of RHA still did not completely dissolve with high concentration of NaOH. Therefore, the formation of aluminosilicate gel between RHA and alkaline activator in this work is variable, depending on the reactivity, concentration and type of activators being used.

Overall, by looking from graph in Fig. 1, reveals that water is extremely penetrate through the geopolymer network. The earlier trend is similar to the trend on water absorption for polymer. High water absorption tend to increase the sample swelling and subsequently increase the number of cracking in geopolymer sample. Thus, more water could penetrates along the micro-cracking interface which creating swelling stresses and finally broke the sample [9].
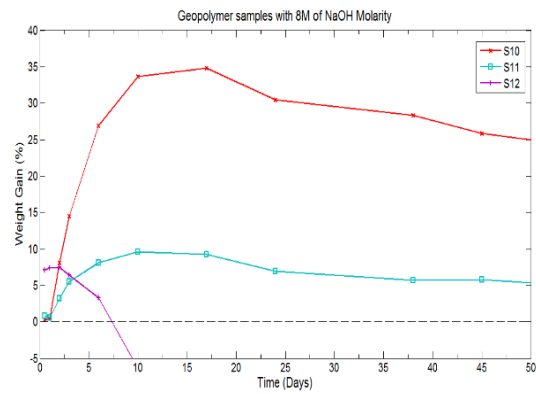
However, interestingly found that some of the geopolymer sample weight in this work start to decrease after remain soaking in water for certain number of days. This indicate that the geopolymer still undergo geopolymerization process which can be due to decrease in the number of microcracks [10]. Presence of water tend to accelerate the polycondensation process of geopolymer sample by continual dissolution of residual raw materials and continue hydrolysis process of Al^{3+} and Si^{4+} [11].

The variation in percentage weight gain of geopolymer samples is shown in Table 3. In Day 1, sample S23 shows the lowest weight gain. However, as prolonged the absorption time to 5 days, the weigth gain increased to 13.36% which is about 50 times higher than intial weigth gain. Comparatively, sample S05 showed slightly high weight gain in Day 1, and the increment is only for about 4 times compared to the initial weight gain.
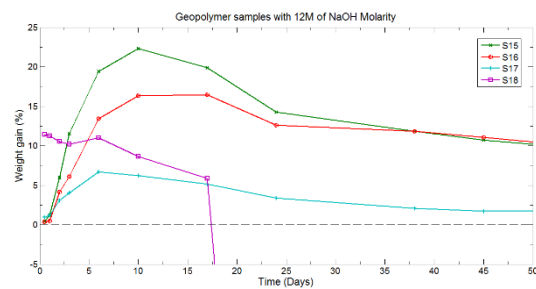
Geopolymer produces with high concentration and high ratio of $NaOH/Na_2SiO_3$ such as for sample S23, not only has high amount of sodium content, but also increase in silicate content. Therefore, the crosslink reaction in geopolymer will be disrupted due to the presence of excess sodium silicate which hinders the water evaporation and structure formation of the geopolymer [12]. Interestingly, for all samples, the weight gain start to decrease after 20 days. It indicates that geopolymerization process still take place in which the chains and branches are still forming. In the early stage of the geopolymerization, the pores are large and more water can be absorb through this pores [13]. Later, as the chain and braches continuously forming, the resulting microstructure of geopolymer will be come denser.
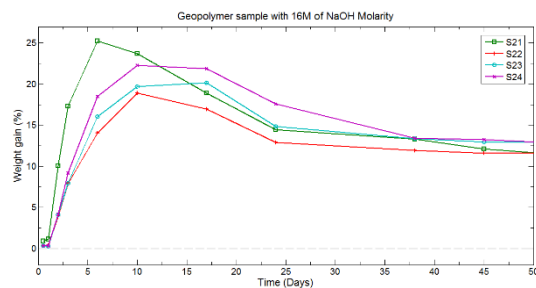
(a)

(b)

(c)

(d)

**Fig. 1. Effects of water absorption on different
geopolymer samples produced with different NaOH concentration**

Table 3. Water absorption for geopolymer samples.

Ratio S/L	NaOH Molarity	Sample	Percentage Weight Gain (%)						
			Day 1	Day 5	Day 10	Day 20	Day 30	Day 40	Day 50
0.5		S02	-	-	-	-	-	-	-
1.0	4M	S03	0.35	8.77	8.62	3.85	2.10	0.92	0.34
		S04	0.28	9.83	14.14	12.33	9.59	8.42	8.05
1.5		S05	1.43	4.88	6.32	4.83	4.40	3.96	4.02
		S06	3.14	6.07	5.57	2.93	1.36	0.16	-
0.5		S08	-	-	-	-	-	-	-
1.0	8M	S09	-	-	-	-	-	-	-
		S10	0.42	22.77	33.66	32.92	29.52	27.60	24.94
1.5		S11	0.52	7.26	9.64	8.27	6.42	5.72	5.36
		S12	7.40	4.34	-6.31	-	-	-	-
0.5		S14	-	-	-	-	-	-	-
1.0	12M	S15	1.27	16.76	22.30	17.47	13.22	11.52	10.20
		S16	0.47	10.99	16.31	14.78	12.25	11.59	10.47
1.5		S17	1.17	5.81	6.22	4.39	2.81	1.97	1.69
		S18	11.24	10.71	8.65	-	-	-	-
0.5		S20	-	-	-	-	-	-	-
1.0	16M	S21	1.11	22.62	23.70	17.02	13.97	12.95	11.65
		S22	0.36	12.01	18.89	15.24	12.49	11.82	11.57
1.5		S23	0.26	13.36	19.69	17.88	14.22	13.26	12.89
		S24	0.29	15.40	22.28	20.05	15.79	13.35	12.97

Figure 2 shows the images on the samples surface after soaking in water for 50 days. Some of the samples were found to be dissolved when soaking in water. These samples are S02, S08, S09, S14 and S20. The dissolve samples are produce with composition of 0.5 ratio of RHA to AA and 0.5 ratio of NaOH to Na_2SiO_3 in any NaOH concentration ranging from 4M to 16M. However, as the ratio of RHA to AA increase to 1.0, the samples were found to be remain intact except for sample S09, which is found to be dissolved after soaking in water. Increase in RHA to AA ratio, reduce the water content in geopolymer during geopolymerization process. Moreover, curing might affect the properties of geopolymer in which the loss of moisture rapidly occurred on the surface while and lead to the formation of crack on the geopolymer surface [14].

Al Bakria et al. [15] mentioned in their work that curing temperature tend to affect as well the performance of the geopolymer. They added that curing at high temperature, lead to the substantial loss of moisture as geopolymer reaction need presence of water in order to develop good strength. Figure 2 also revealed that S12 and S18 in this work were found to be broken after soaking for 50 days in water. Combination of high RHA to AA ratio and high NaOH/Na_2SiO_3 ratio for sample produce with 8M and 12M NaOH indicates that this sample is highly brittle. Use of high alkaline solution, tend to increase the water absorption in geopolymer sample. In addition, presence of high amount of Na_2SiO_3, tend to produce geopolymer with large pore size [16]. Thus, diffusion of water molecules inside the micro gaps between the geopolymer chain or due to the capillary transport between gaps or voids presence in geopolymer, increase the crack propagation process which lead to the brittle failure of sample after soaking.
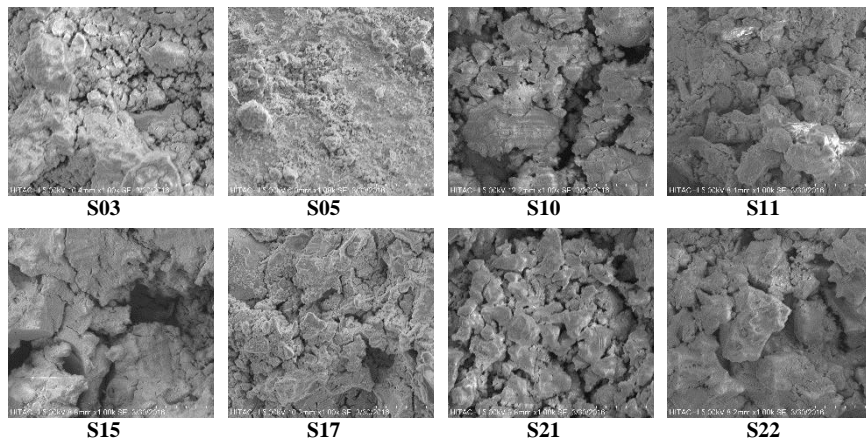
Fig. 2. Samples condition after the water absorption test.

3.2. Microstructural analysis

The microstructure of geopolymer sample after water absorption analysis are shown in Fig. 3. Most of the sample shows severe geopolymer cracking and degradation as can be characterized by the appearance of cracks and gaps in the sample. However, sample S05 did not show significant presence of cracks compared to others. Moreover, by looking at the sample structure for sample S05 after soaking as shown in Fig. 2, the sample structure still remain intact with less degradation effects occurred on the sample. This indicate that formulation composition for sampel S05 can produced dense or compact geopolymer. Processing of geopolymer with high alkaline concentration is known to accelerate geopolymerization process. However, with too much excess of OH- concentrations or alkalinity, tend to create early precipitation of aluminosilicate gel. Thus, reduce the interaction between the rice husk ash particle with alkaline solution. In addition, mixing with high concentration of alkaline solution, increase the viscosity of the geopolymer, reduce the workability and subsequently, inhibit the geopolymerization process. Moreover, presence of excessive ions interupt with the chain mobility and reaction with reactive species [17].

S03	S05	S10	S11
S15	S17	S21	S22

Fig. 3. The SEM images of geopolymer samples.

4. Conclusions

In this study, different concentrations of NaOH were studied on producing geopolymer based on rice husk ash. Initially geopolymer sample produce with high alkaline activated content (16M), have high tendency to absorbed water for about 50 times. On the other hand, for the geopolymer produce with low alkaline activated content (4M), the initial water uptake is approximately 4 times. Thus, presence of high amount of silicates and OH- from alkaline activator solution gives significant effects on the geopolymerization process, in which the excessive ions tends to disrupt the chain reaction process between rice husk ash and alkaline solution. In further, the geopolymer samples could be able to strengthen to reduce the structure degradation when in contact with water by improving the mixing ratio of the geopolymer samples. By doing further studied and research on the ratio of Si and Al when mixing the geopolymer samples might able to produce the optimum ratio of geopolymer samples.

Acknowledgement

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