Rice husk ash (RHA) based geopolymer mortar incorporating sewage sludge ash (SSA)

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Abstract. Geopolymer based cementitious materials were produced to reduce or completely eliminate the use of cement in concrete in which could be incorporated with waste materials. In this study, rice husk ash (RHA) which is a waste having rich in silica content after burnt was intended to be used as based geopolymer. Besides, sewage sludge ash (SSA) was incorporated with RHA producing geopolymer mortar in which also having pozzolanic element of Si and Al. Geopolymerisation requires Si and Al elements to react with highly alkaline solution to produce geopolymeric material. Therefore, combination of RHA and SSA will be possible solution as base geopolymer mortar in order to provide Si and Al. The effect of SSA inclusion was investigated under different sodium hydroxide (NaOH) molarity and curing conditions to the strength development. NaOH and sodium silicate were used as activator with ratio of 1:1 and the solution to ashes ratio of 1:1 was used. Compressive strength was tested at 7, 14 and 28 days. The results showed that the geopolymer mortar made of SSA replacement exhibited higher compressive strength with reference to those made of RHA (control sample). In addition, the results showed that geopolymer mortar specimen containing 15% of SSA replacement activated with 8M NaOH solution gave the highest strength recorded 15.0MPa in oven curing condition (60°C for 24 hours). As conclusion, SSA up to 20% replacement has potential to be used in producing geopolymer as replacement alternative to RHA.

1. Introduction

In recent years, there are numerous studies conducted on the geopolymer mortar that totally replace cement to get considerable strength. In current scenario, fly ash (FA) is usually been used in producing geopolymer mortar which are rich in alumina and silica content in chemical composition of FA [1-5]. However, in this study, rice husk ash (RHA) which is usually burnt was chosen to be used as the based materials for geopolymer. Basically, a pozzolanic RHA with high content of SiO₂ can be formed through a controlled firing process [6]. The chemical composition of RHA has been identified to have high SiO₂ content in which this component could help in forming a good binder for the geopolymer. However, due to the limited content of Al₂O₃ found in the RHA from total mass, SSA has been suggested for the combination in producing the based geopolymer with high content of Al₂O₃.

Aluminosilicate polymer also known as geopolymer are aluminosilicate network structure that form between the reaction of solid amorphous aluminosilicate (Si-Al) with highly concentrated alkali hydroxide or silicate solution to activate reactive Si and Al [7-8]. Knowing that, geopolymerisation process needs silica alumina element to react with highly alkali metal hydroxide and/or alkali silicate materials to mediate the reaction [9]. This geopolymer consists of repeating tetrahedral unit of Si-O-
Al-O. Dissolution of silica and alumina by alkali metal salt and/or hydroxide was necessary for the polymerisation process. In addition, they react as catalyst in the reaction of condensation. Polymerization of individual silica and alumina elements from their sources with highly alkaline solution will form a highly reactive gel phase.

Moreover, study conducted by Mohd Mustafa [10], indicated that curing process and alkaline activator used in geopolymerization were the most important factors that affect the strength performance of geopolymer itself. It is in line with the study conducted by Kamhangrittirong [11] whom also stated that sodium hydroxide molarity and curing temperature could affect the strength performance of geopolymers [2,9,12-14]. The question whether increasing the molarity of sodium hydroxide and applying heat to the RHA and SSA blended geopolymer mortar as a means of curing could increase the strength of the geopolymer. What is the most suitable proportion of RHA to SSA should be used in producing geopolymer mortar is another question raised that lead to the implementation of the present work. Therefore, the intention of this research is to determine the most suitable proportion of combining RHA and SSA in producing geopolymer utilizing various NaOH molarity (4M,6M,8M) and two curing regimes (air and oven curing).

2. Materials and Methods
2.1. Characterization of rice husk ash (RHA) and sewage sludge ash (SSA)
In this research study, rice husk was collected from Bernas factory Kuala Selangor, Malaysia. Rice husk undergone uncontrolled burning in range of 500°C to 600°C for 24 hours and followed by grinding using Los Angeles machine in producing RHA. Meanwhile, sewage sludge cakes were obtained from the Wastewaster Treatment Plant, KLIA Sepang, Malaysia. Dried sludge cake was burnt at temperature of 900°C for 5 hours in the gas furnace followed by grinding using Ball Mill machine to obtain small particle in size of SSA.

2.2. Preparation of geopolymer mortar
There are three (3) different molarities (M) of NaOH used in this study as activated solution for preparing geopolymer mortar which are 4M, 6M and 8M meanwhile sodium silicate with concentration ratio of \( \text{SiO}_2: \text{Na}_2\text{O} \) of 2.5:1 remains constant for all mixtures. NaOH pellets were dissolved in water to produce the solution. Table 1 shows the materials and mix proportion in kg/m\(^3\) used in preparation of RHA geopolymer mortar. Meanwhile, four (4) different replacement level of SSA replacing RHA were namely as S5 (5%), S10 (10%), S15 (15%) and S20 (20%) of the total weight of source materials were adopted. Plain RHA based geopolymer mortar was used as a control mixture (S0). The geopolymer mortar was cast into cubes of 50 mm x 50 mm x 50 mm greased metal mold using vibration table methods. Afterwards, the specimens were cured in two types of curing conditions namely; in air curing with the average of 25°C to 30°C and in oven curing with 60°C for 24 hours.

| Mix | Source materials | Sand | NaOH | \( \text{Na}_2\text{SiO}_3 \) | Liquid/solid\(^\text{a}\) ratio (mass) | NaOH/\( \text{Na}_2\text{SiO}_3 \) ratio (mass) |
|-----|----------------|------|------|----------------|-----------------|----------------|
| S0  | 502            | 0    | 1004 | 251          | 251             | 1.0            | 1.0            |
| S5  | 477            | 25   | 1004 | 251          | 251             | 1.0            | 1.0            |
| S10 | 452            | 50   | 1004 | 251          | 251             | 1.0            | 1.0            |
| S15 | 430            | 75   | 1004 | 251          | 251             | 1.0            | 1.0            |
| S20 | 402            | 100  | 1004 | 251          | 251             | 1.0            | 1.0            |

\(^{a}\) Solid included RHA and SSA.
2.3. Procedure of mixing
Combination of NaOH with sodium silicate solution was used to dissolve the silica and alumina of the RHA and SSA to activate geopolymerisation process. NaOH and sodium silicate solutions were mixed together for 24 hours prior to mortar mixing to ensure the reactivity of solution was completed. Next, the RHA and sand were dry mixed for 1 minute. Lastly, NaOH and sodium silicate solution was added into the dry mix. The mixture was mixed for 3 minutes.

2.4. Tests
After a curing process, all the specimens were stored at room temperature until the tests were conducted. At 7, 14, and 28 days, the geopolymer mortar specimens were tested compressive strength as according to BS EN 12390-3:2002. The average results of three identical specimens for each group was taken. While for the chemical analysis, the specimens given maximum strength at 28th days were measured using X-Ray Diffraction (XRD) test.

3. Results and discussions
3.1. Chemical composition of material by X-ray Fluorescence (XRF)

| Chemical Composition (%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | K$_2$O | SO$_3$ | Na$_2$O |
|--------------------------|--------|-------------|-------------|-----|-----|-------|--------|--------|
| RHA                      | 74.13  | 0.13        | 0.32        | 0.65| 0.66| 2.87  | 0.53   | 0.03   |
| SSA                      | 39.21  | 19.71       | 6.59        | 2.30| 1.25| 2.27  | 2.63   | 0.24   |

Table 2 shows the chemical composition of RHA and SSA. It can be seen that the total of silicone dioxide (SiO$_2$), aluminium oxide (Al$_2$O$_3$) and ferum oxide (Fe$_2$O$_3$) of RHA is 74.48% which can be classified as Pozzolan Class F and hence satisfying the requirement of ASTM 618-12a which stipulates minimum of 70%. Scanning electron microscope (SEM) was used to investigate the morphology of the RHA particles and it is illustrated in Figures 1a and 1b. It is observed that the RHA particle consisted of coral and skeletal irregular shape [6] and also angular and multilayered surface [15]. Meanwhile, the total major element of SSA are silicone dioxide (SiO$_2$), aluminium oxide (Al$_2$O$_3$) and ferum oxide (Fe$_2$O$_3$) is 65.51% which can be classified as Pozzolan Class C, hence, satisfying the requirement needed in ASTM C618-12a which stipulates minimum of 50%. In addition, aluminium oxide content in the sewage sludge ash was 19.71% which is having potential in activating geopolymerisation process. Figures 1c and 1d show the micrograph of SSA particles, having a very irregular in shape, with porous cellular surfaces in which lead to high in water absorption and contributed to increase the water demand to the mortar [16]. Figure 2 depicts the particle size distribution of RHA and SSA. It can be deduced that SSA is having smaller size in particles than RHA recorded mean size of 4.248µm and 30.36µm for SSA and RHA, respectively. The specific surface area of SSA was 3.892m$^2$/g while RHA was 0.6859m$^2$/g. The higher value of specific surface area explaining the requirement of water in the mixture [9].

![Figure 1: SEM photo of: (a) RHA under 200x (b) RHA under 3000x (c) SSA under 200x and (d) SSA under 3000x magnification](image-url)
Figure 2. The particle size distribution of RHA and SSA used in the present study.

Figure 3. XRD pattern for: (a) RHA and (b) SSA.

Figure 3 shows the XRD pattern of ground RHA and SSA with a major phase of SiO$_2$ based on Cu radiation. XRD pattern for RHA scattered gradually towards the peaks of approximately 502 count of intensity and the location of the highest hump was also detected at range of 15° to 40° diffraction angle at (2θ) which is equal to 22°. Figure 3a shows the diffraction angel at 20.75°, 26.8° and 40.2° correspond to Quartz (Q). The other peaks which is at 21.7°, 28.9°, 31.2° and 36.0° represent to Cristobalite (C) phase. Cristobalite shows the sharp peaks which is represent the crystallization of silica and also present as a major constituent in the RHA as displayed in Table 2. This broad hump occur in XRD pattern RHA was representing the amorphous phase due to broad peak at range between 15.8° and 27.0° (2θ) [15,17-18]. Meanwhile, as in Figure 3b displays the pattern of SSA particles which indicated the silica content of the ash at approximately 2193 counts at diffraction 2θ angle which is equal to 27°. The location of highest hump detected at range of 20° to 40° (2θ) and represent the amorphous phase. The major component that identified in the XRD pattern of SSA are quartz at 26.2° followed by 20.8°, 36.5°, 51.2° and 60.0° at 2 theta diffraction angles. The minor component shows at diffraction angle of 22.0°, 24.0°, 33.0° and 35.7° correspond to hematite (H) followed by
25.2° and 31.2° indicates to anhydrite (N). Moreover, albite (A) mineral also detected at diffraction angle of 27.9° and 35.7° 2θ. The amorphosity or crystallinity formation of silica in materials depends on the burning method and temperature of burning [19-20]. The RHA and SSA were comprised mainly of amorphous phase in which having large amount of SiO₂ as agreed in chemical composition shown in Table 2. Therefore, these two materials have potential as source material for making geopolymer mortar.

3.2 Compressive Strength

The compressive strength of five (5) series of geopolymer mortar specimens made of different molarities of NaOH and cured in two (2) conditions are shown in Figure 4. By replacing RHA partially by SSA up to 20%, it gives significant effect on the strength development of the resulted geopolymer mortars as compared to those of plain RHA based geopolymer mortar (control sample). It is because RHA is low in alumina component compared to SSA which is having higher alumina component. By replacing RHA with SSA, as a result increase the alumina component in the matrix. In geopolymerisation reaction, alumina will be dissolved easily than silica component contributes to a higher condensation rate between silicate and aluminate resulting in higher rate of strength development at early age. Alumina component in SSA will allow to make more Al (OH)₃ species in the geopolymer matrix resulting in high rate in strength development [9,18]. Nevertheless, the inconsistent ratio of Si/Al throughout the geopolymerization due to changes of initial Si/Al content by replacing several replacement levels of SSA content affect the compressive strength trends. The gradual increment of Si content by SSA replacement, further increases the silicate species for condensation and causing domination of reaction between silicate and silicate species. This domination of silicate species will tend to slower the rate of condensation and consequently into gradual hardening. In this case, by increasing the SSA content in the geopolymer mortar, it delays the gaining of ultimate compressive strength. In this study, replacing of SSA at 15% replacement exhibits higher value of compressive strength regardless the molarity and curing conditions adopted.

![Figure 4. Compressive strength due to SSA replacement and two curing conditions at: (a) 4M, (b) 6M and (c) 8M of NaOH](image_url)
Furthermore, the specimens that prepared by different molarity of NaOH exhibits different pattern of compressive strength. By increasing the NaOH molarity, the strength of geopolymer mortar attained also increased. It showed that those specimens composed of 8M give the highest in strength as compared to those made of 4M and 6M. The compressive strength of RHA based geopolymer mortar incorporating with SSA is expected to increase with increasing NaOH molarity because of the Si and Al are dissolved more aggressive in high molarity solution. However, further increase in molarity will delay the condensation in the structure and may break the geopolymer matrix structure. With high OH concentration, it will accelerate the RHA and SSA particle to dissolve and accelerates geopolymerisation process as well. It was observed that geopolymer mortar activated using 8M solution gave the highest strength marked 15.0 MPa cured in oven for 28 days as compared to those made of 4M and 6M. While, the usage of low alkaline solution resulting on low and weak chemical reaction [21]. Additionally, the specimens that cured in oven with 60°C for 24 hours showed higher in strength value as compared to specimens that cured in air curing condition regardless of the replacement levels of SSA. Curing temperature do give effect on the hardening and geopolymerisation process in the geopolymer matrix by accelerating the reaction. The accelerated reaction enhances the bonding between aggregate and geopolymer matrix and thus strengthened the geopolymer mortar specimens [22].

3.3. X-ray Diffraction (XRD)

Figure 5. The XRD pattern for 15% SSA replacement in RHA based geopolymer mortar prepared by: (a) 4M, (b) 6M and (c) 8M at 28 days for oven curing conditions
Figure 5 depicts the XRD pattern of geopolymer mortar containing 15% SSA replacement which attained the highest strength when cured in oven for 28 days prepared using 4M, 6M and 8M NaOH solution. There is a shoulder diffraction angle (2θ) ranging in 16° to 30° and 24° to 50° for RHA and SSA, respectively. However, activation of RHA and SSA particles with alkaline solution, resulting in shifted of range from 20° to 40°, which has been identified as diffraction patterns of geopolymer [11]. The formation of new gel phase depends on the OH concentration in sodium hydroxide [23]. By increasing the molarity of NaOH, new crystalline silicate and aluminosilicate compound created in the matrix gel. It is indicated that geopolymer mortar made of 8M of NaOH relatively having high level of geopolymerization and consequently higher strength was obtained. Figure 5 shows similar XRD pattern for geopolymer mortar made of 4M, 6M, and 8M NaOH slightly different pattern from raw RHA and SSA. There are no new peaks detected for all specimens at range 2θ (degrees). However, there is an increase in intensity inferring the materials were dissolved in geopolymeric materials as also agreed with study conducted by Alias Tudin et al. [18]. Quartz and cristobalite were the major crystalline phase presented which is the main mineral formed that responsible in the strength development of geopolymer mortar. It is noted that there is a number of quartz and cristobalite in RHA and SSA remained in the product which are not totally dissolved by alkaline activator. Nevertheless, there is increasing in the peak intensity indicating that parent materials were not totally dissolved into polymeric materials. The XRD pattern for all geopolymer mortar samples displayed a diffuse halo at 2θ diffraction angle in between 20°- 40° representing the typical pattern in geopolymer gel. The differences on the peak intensity would affect the strength obtained. With increasing in crystalline intensities, the compressive strength obtained would also increase. It is in line with the compressive strength result obtained. Based on analysis made at diffraction angle of 27.5°, 42.5°, 45.8° and 57.2°, most the geopolymer sample correspond to zeolite formed [5,23] which is beneficial to the strength development for geopolymer mortar.

4. Conclusions
Based on the results obtained, it can be concluded that combination of RHA and SSA demonstrated higher strength than those made of only RHA based geopolymer mortar (control sample). For all series that containing SSA, 15% SSA replacement level marked the highest compressive strength. Increase the molarity of NaOH, increase the compressive strength of the resulted geopolymer mortar. In this case, those specimens made of 8M NaOH solution depict the highest strength. It is deduced that the specimens that cured in oven with 60°C for 24 hours exhibits higher in strength as compared to specimens that cured in air condition. It is noted that 15% of SSA replacement and made of 8M NaOH solution gave the highest strength recorded 15.0MPa at 28 days of oven curing (60°C for 24 hours). Thus, it is concluded that combination of RHA and SSA contributes to strength development in geopolymer. The XRD pattern observed for all geopolymer mortar samples display a diffuse halo at 2θ diffraction angle in between 20°- 40° referring mortar has undergone geopolymerization process was taken place and also explaining the compressive strength development by measure the intensities value in XRD graph.

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