The effect of alkali activation solutions with different water glass/NaOH solution ratios on geopolymer composite materials

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Abstract. In this study, geopolymer materials were produced from fly ash (FA) supplied from İşken Sugözü Thermal Power Plant located in Adana, Turkey. FA and Rilem Cembureau Standard Sand were used together with the ratio of 0.5. At first, two different alkaline solution/material ratio (FA+standard sand) (L/M) were selected as 0.2 and 0.4 for the design parameters. In the production of geopolymer composite material, sodium silicate (Na₂SiO₃) and sodium hydroxide (12 M NaOH) were used together within the ratio of 1, 1.5, 2, 2.5 and 3 by weight, respectively. A totally of 20 mixes were cured at 70 and 100 oC for 24 hrs, respectively and thereafter kept in room temperature until testing age. Physical characteristics of hardened mortar were determined via the bulk density, water absorption and porosity values at 28 days while the strength of geopolymers was obtained on the results of compressive strength and flexural strength tests conducted at 7, 28 and 90 days. Considering the testing parameters, geopolymer material with the highest compressive strength was found as 76.0 MPa (28-days) on the mixture produced with L/M ratio of 20% by weight; the alkaline solution consisted of a mixture of Na2SiO3 and 12 M NaOH in weight ratio of 2 by curing at 70 oC for 24 hrs. However, test results showed that there was an optimum limit for the alkaline solution ratio, such that exceeding this limit gave the reverse effect for the strength characteristics of the geopolymer material.

1. Introduction

The awareness of sustainable development in the world has led to the evaluation of the environmental effects as well as the technical properties of the construction materials in the design. Conventional concrete produced with ordinary Portland cement (OPC) is the most widely used material in the construction sector. After mining and grinding raw materials that include limestone and clay, the Portland cement can be produced via a sintering temperature as high as 1500 °C in a cement kiln for desired strength characteristics. High energy consumption is required for the grinding of clinker as well as the production stage. Additionally, the burning of fossil fuel used in the production results high levels of carbon dioxide (CO₂) emissions associated warming of the atmosphere as well as the small amount of other harmful gases. It is reported that cement production for 1 ton causes approximately 0.9 ton of CO₂ emission [1-2]. Due to the fact that the annual cement production in the world is over 3.5 billion tones and the cement sector is responsible for 5-8% of the man-made CO₂ emissions, the researchers have been forced to search the new construction materials as an alternative to conventional concrete in the terms of the environmental effects [2-3].
Fly ash (FA) is driven out of the boiler with flue gases in coal-fired power plants and then generally captured from flue gases by some special equipment (e.g. electrostatic precipitators or other particle filtration equipment) before the flue gases reach the chimneys. The high quantity of FA is currently disposed to landfills by creating a threat to the environment due to the effects to ground water as well as biodiversity [3-4]. The compositions of FA vary noticeably depending on the source of the coal being burned, but the main components are SiO$_2$ (40-60%), Al$_2$O$_3$ (20-30%), Fe$_2$O$_3$ (4-10%) and CaO (5-30%) [5]. In order to comply with sustainable development concept, it is very important to minimize the negative environmental impacts of waste materials. On the other hand, FA that is a by-product from thermal power plants can be used as a supplementary cementitious material through the pozzolanic reaction instead of OPC. Another alternative which has been discussed as a substitute for OPC concrete is the geopolymer concrete that can be easily produced with FA by synthesizing pozzolanic compounds or aluminosilicate source materials with highly alkaline solutions [6-7]. Geopolymers consume significantly less energy and reduce the emission of greenhouse gases. The use of FA as the cementitious source in the manufacture of geopolymer concrete has been intensively investigated for not only mechanism of geopolymerization but also mechanical properties of the resulting concrete. It has been shown that in general Class-F FA that is the one of the most suitable widely used aluminum silicate sources for the production of geopolymers as the final product exhibits superior mechanical and durability properties when exposed to aggressive media and under thermal loading [8-10].

The objective of this study is to examine the potential of FAs that are supplied from İskendere Sugözü Thermal Power Plant located in Adana, Turkey in the manufacture of geopolymer and develop a FA-based geopolymer composite material with its enhanced physical-mechanical properties. In this study, FA and Rilem Cembureau standard sand (CEN reference, as fine aggregate) were used with the ratio of 0.50. Two different alkaline solution/material ratio (FA+standard sand) (L/M) were selected as 0.20 and 0.40 for the design parameters. In the production of geopolymer composite material, sodium silicate (Na$_2$SiO$_3$) and sodium hydroxide (12 M NaOH) were used together within the ratio of 1, 1.5, 2, 2.5 and 3 by weight, respectively. This paper presents the findings of various laboratory tests on the behavior of geopolymers to be used as composite materials.

2. Materials and Test Methods

2.1 Materials

An ASTM C618[11] Class-F FA supplied from İskendere Sugözü Thermal Power Plant in Adana (Turkey) was used as a geopolymerizing material in this study. Chemical compositions of FA obtained from X-ray fluorescence (XRF) test were presented in Table 1. The specific gravity of FA was obtained as 2.25. Rilem Cembureau standard sand complied with TSE EN 196-1 [12] specification was used in the production of mortar mixtures. Sieve analysis of this special sand given in Table 2 is found to be in agreement with the limits of standard. The activator was a combination of Na$_2$SiO$_3$ known as water glass or liquid glass and 12 M NaOH. The Na$_2$SiO$_3$ solution was consisted of Na$_2$O=14.7%, SiO$_2$=29.4% and H$_2$O=55.9%. Additionally, 12 M NaOH solution was prepared by dissolving of NaOH existing in the form of pellets.

| Oxides (%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | Na$_2$O | MgO | K$_2$O | SO$_3$ | BET (m$^2$/g) | LOI (%) |
|------------|--------|------------|-------------|-----|---------|-----|-------|------|-------------|--------|
| FA         | 62.28  | 21.46      | 7.01        | 1.53| 0.26    | 2.37| 3.81  | 0.07 | 2.26        | 1.78   |
Table 2. Properties of Rilem Cembureau standard sand.

| Diameter of sand grain (mm) | 0.08 | 0.16 | 0.5 | 1.0 | 1.6 | 2.0 |
|-----------------------------|------|------|-----|-----|-----|-----|
| Remaining (%)               | 99   | 87   | 72  | 34  | 6   | 0   |
| Limits of specification (%) | 99±1 | 99±5 | 67±5| 33±5| 7±5 | 0   |

2.2 Mix Design
A total of 10 mixes were designed in which different L/M and Na$_2$SiO$_3$/NaOH ratios were utilized, respectively. The FA/sand ratio in the geopolymer mortar was kept constant at 0.50 (400/800). At first, two different L/M ratios were selected as 0.20 and 0.40. In addition, Na$_2$SiO$_3$ and 12 M NaOH solution were used together to support the dissolution of solid FA particles within the ratios of 1, 1.5, 2, 2.5 and 3 by the weight, respectively. Therefore, the ratio of SiO$_2$/Na$_2$O was changed between 0.57-1.09 in each alkali activation solution. The mixing ratios of geopolymer mortar are presented in Table 3.

Table 3. Mix proportion of geopolymer mortars.

| FA (g) | Standard Sand (g) | Alkaline Solution/Materials Ratio (L/M) | Na$_2$SiO$_3$/NaOH Ratio | NaOH (g) | Na$_2$SiO$_3$ (g) | Total Water/Materials Ratio |
|--------|-------------------|----------------------------------------|--------------------------|----------|------------------|----------------------------|
| 400    | 800               | 0.20                                   | 1                        | 120      | 120              | 0.18                       |
|        |                   |                                        | 1.5                      | 96       | 144              |                            |
|        |                   |                                        | 2                        | 80       | 160              |                            |
|        |                   |                                        | 2.5                      | 68       | 172              |                            |
|        |                   |                                        | 3                        | 60       | 180              |                            |
|        |                   |                                        | 0.40                     | 1        | 240              | 0.20                       |
|        |                   |                                        | 1                        | 240      | 240              |                            |
|        |                   |                                        | 1.5                      | 192      | 288              |                            |
|        |                   |                                        | 2                        | 160      | 320              |                            |
|        |                   |                                        | 2.5                      | 136      | 344              |                            |
|        |                   |                                        | 3                        | 120      | 360              |                            |

The mixing procedure used for the FA-based mortar is the same as the cement-based mortar. In the first stage of the mortar formation, FA and standard sand were mixed with a mixer for 30 seconds to obtain homogeneity. Pellets of NaOH were dissolved in the water to obtain the required concentration before mixing. Then, Na$_2$SiO$_3$ and 12 M NaOH were mixed for the desired content of the alkaline solution and added to the mixture. The workability of fresh geopolymer mortar was tested with respect to ASTM C1437 [13]. The target slump flow diameter determined as 14±2 cm was obtained by producing the different test batches for each type of mortar. At the end of the production, the prepared mortar immediately fed into molds with the dimensions of 40x40x160 cm and vibrated until getting full compaction. Finally, geopolymer mortars were cured at 70 and 100 oC by using the protecting cover to prevent evaporation of water, for 24 hrs, respectively. Thus, a total of 20 different hardened geopolymers were obtained. As seen in Figure 1, the hardened samples were kept under room temperature until the testing age for the physical and mechanical tests.
The hardened geopolymer mortars were coded based on the design parameters such as L/M ratio, curing temperature and Na$_2$SiO$_3$/NaOH ratio. For example, when the geopolymer was manufactured with the ratios of L/M=0.40, Na$_2$SiO$_3$/NaOH=1 and cured at 70 °C, this mixture was denoted as 40FA-70-1.

2.3 Experimental Study
The bulk density, water absorption (by mass) of the hardened mortars were measured according to ASTM C642 [14] while TS EN 772-4 [15] was used to determine the porosity of samples at 28 days. Compressive and flexural strengths of geopolymer mortars were tested with in the line of ASTM C 349-14 [16] and ASTM C 348 [17] at 7, 28 and 90 days, respectively. The average of six measurements for each test is reported at each testing age.

3. Test Results and Discussion
The variations of test results for physical characteristics of geopolymer are given in Figure 2. As seen in Figure 2, the bulk densities at 28 days were changed between 1820-2079 and 1798-2012 kg/m$^3$ for hardened mortars cured at 70 and 100 °C for 24 hrs, respectively. Increasing the ratio of Na$_2$SiO$_3$/NaOH resulted an increment for the bulk density of the specimens cured at 70 °C while the bulk density of geopolymers cured at 100 °C were decreased by the increased ratio of Na$_2$SiO$_3$/NaOH. This may be attributed to fact that the presence of aggregate induced thermal expansion between the aggregate and paste, thus increasing curing temperature as well as Na$_2$SiO$_3$/NaOH ratio causing the disintegration in the polymer network as well as the expansion of specimens [18].
Figure 2. Bulk density of hardened geopolymers at 28 days.

Figure 3 and 4 shows the results of water absorption and porosity in units of percent (%) for geopolymer mortars at 28 days, respectively. Decreasing porosity reduced the water absorption of geopolymers as a result of decreasing pore size. It was observed that geopolymer mortar specimens produced with the ratio of Na$_2$SiO$_3$/NaOH up to 2 and cured at 100 °C resulted lesser values of water absorption and porosity when compared to one’s cured at 70 °C. 40FA-70-1 specimen had 24.55% water absorption and 38.43% porosity whereas 20FA-100-2 showed comparatively lower corresponding values of 8.31% and 17.0%, respectively. This conclusion was supported by the researchers showed that high dissolution of the FA particles in the mixture obtained by higher alkali content resulted in denser microstructure in geopolymers [19-20].

Figure 3. Water absorption of hardened geopolymers at 28 days.
Figure 4. Porosity of hardened geopolymers at 28 days.

Compressive and flexural test results with respect to Na$_2$SiO$_3$/NaOH ratio are indicated in Figures 5 and 6 at 7, 28 and 90 days, respectively. As observed from Figures, the testing age does not have an important effect on strength characteristics of geopolymer after the curing process was completed [18]. Increasing the ratio of Na$_2$SiO$_3$/NaOH gave an increment of strength characteristics up to an optimum point (Na$_2$SiO$_3$/NaOH=2). Generally, it was accepted that higher concentration gave the better strength. But, there was an optimum limit for the alkaline solution ratio, such that exceeding this limit gave the reverse effect for the strength characteristics [3-21]. Thus, the highest compressive and flexural strength values were found 76.0 MPa and 10.5 MPa for 20FA-70 at 28 days, respectively. However, the compressive and flexural strength were reduced by the increasing ratio of L/M. This effect can be explained by Yang et al. [22] stated that similar to hydraulic Portland cement paste, higher water-to-cementitious-materials ratio can cause a reduction on strength values. Moreover, the hardened mortars designed with the ratio of L/M=0.40 and cured at 70°C had the lowest compressive and flexural strength. This result agrees with the finding of Bhowmick and Ghosh [23] showed that when higher sand content was used in the geopolymerization process, the quantity of the geopolymer gel may not be sufficient to bind all loose aggregates; thus, the reduction in strength was observed. Additionally, for the same ratio of Na$_2$SiO$_3$/NaOH, increasing curing temperature caused deterioration in compressive and flexural strength. Similarly, Atiş et al. [24] indicated that the available water in the mix instantly vaporized by heat curing process before dissolution of FA in the alkaline environment.
Figure 5. The variations of compressive strengths with respect to Na$_2$SiO$_3$/NaOH ratio for hardened geopolymers.

Figure 6. The variations of flexural strengths with respect to Na$_2$SiO$_3$/NaOH ratio for hardened geopolymers.
4. Conclusions
The following conclusions can be drawn from this experimental study:

- Workable geopolymer mortar with an acceptable strength can be manufactured by activating locally available Class-F FA with different alkaline solution content comprised of Na₂SiO₃ and 12M NaOH solution.
- The bulk density of the specimens cured at 70 °C was increased by the increasing the ratio of Na₂SiO₃/NaOH. However, the increment of curing temperature resulted a decrease for the bulk density due to the thermal expansion of the aggregate in geopolymer matrix.
- Water absorption and porosity values were decreased by the ratio of Na₂SiO₃/NaOH up to 2 as well as the increasing curing temperature.
- Geopolymer mortars had a compressive strength ranged between 11.0-76.0 MPa at 28 days were produced. Increasing the ratio of Na₂SiO₃/NaOH gave an increment of strength characteristics up to an optimum point obtained as 2. Thus, the highest compressive and flexural strength values were found as 76.0 MPa and 10.5 MPa for the mixture with L/M ratio of 0.20 cured at 70 °C at 28 days, respectively. Moreover, the compressive and flexural strength were reduced by the increasing ratio of L/M due to the geopolymer gel can be sufficient to bind all sand in the mixture.
- It can be concluded that geopolymers produced in this study with an acceptable strength could be used in construction sector such as bricks blocks, paving stone or kerbstone as well as prefabricated materials. Geopolymer production not only provides an opportunity to use FA as a binder by alkaline activation but also contributes the environmentally sustainable development by avoiding the disposal problems of FA.

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