Production of geopolymer composites by using different alkaline solution/material ratio

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Abstract. This study reports an experimental program to optimize mix design parameters of fly ash-based geopolymer engineering composites. Fly ash (FA) supplied from Çatalağzı Thermal Power Plant (Zonguldak, Turkey) and Rilem Cembureau Standard Sand were used together with a constant ratio of 0.50 for producing geopolymer. In the first step, two different alkaline solution/material ratio (FA+standard sand) (L/M) were determined as 0.20 and 0.40, respectively. After that, sodium silicate ($\text{Na}_2\text{SiO}_3$) and 12M sodium hydroxide ($\text{NaOH}$) were utilized at a ratio of 1, 2, and 3, respectively. 6 mixtures obtained by using different design parameters were cured at 70 °C for 24 hours, respectively, and then they were stored at room temperature until testing age. While the physical properties of the samples were measured by the bulk density and water absorption tests at 28 days, mechanical properties were tested via the compressive and flexural strength tests at 90 days, respectively.

The results indicated that the highest compressive strength for geopolymer materials was found as 36.5 MPa in the mixture produced with the ratios of L/M=0.2 and Na$_2$SiO$_3$/NaOH=2 (by weight). However, less alkali reaction caused by using excessive activator solutions decreased the strength characteristics of geopolymer.

1. Introduction

The awareness of sustainable development in the world has led to the restructuring of characteristics properties for construction materials in the view of strength requirements as well as environmental impacts. It is known that approximately 4 billion tons of greenhouse gas emissions are emitted from the production of ordinary Portland cement (OPC); this corresponds to approximately 7% of global greenhouse gas emissions [1,2]. The use of industrial wastes such as fly ash (FA), blast furnace slag and silica fume as raw material instead of cement is advantageous both economically and environmentally to reduce the need for OPC [3,4]. In addition to eliminating the use of OPC, the growing concern of sustainable development for green concrete has led to the study of new building materials called as “geopolymers”.

Geopolymer is produced with the composition of binding materials containing large amounts of silica and alumina and activated by the use of alkaline liquid [5,6]. Geopolymer production does not
require the high temperature for the calcination, and also, the geopolymer can be produced from industrial by-products with minimal energy. Thus, compared to OPC production, the amount of greenhouse gas supplied to the environment decreased by 44-64% [7,8]. The desired characteristics of geopolymer is based on the composition of solid raw material depends on the molecular structure, the temperature and duration of the thermal curing or calcination process, and the reaction of the respective chemicals with the required molar mixing. FA is a suitable raw material for the geopolymerization technology obtained from thermal power plants by electrostatic or mechanical deposition of particles for geopolymer production since geopolymerization is linked to the alumina-silicate chain [9]. Komnitsas, (2011)[10] stated that the most common alkali activators used in the production of geopolymer materials are sodium hydroxide (NaOH), sodium silicate (Na$_2$SiO$_3$), and potassium hydroxide (KOH) or potassium silicate (K$_2$SiO$_3$). Komljenović et al. (2010) [11] found that the nature and concentration of the activator is the most dominant parameter in the alkali activation process. Additionally, the degree of hydration reactions can be increased by the alkaline concentration in the geopolymer mix and thus, pore volumes reduces by improving microstructural properties of the C-S-H product [12,13]. Also, Ling(2018) [13] determined that curing temperatures changed between 50-80 °C are widely acknowledged values used for successful geopolymer hydration. However, it was highlighted by the researchers that the concentration of activator has a greater effect on the mechanical strength than those of the curing temperature and time [14-16]. Moreover, Hardjito et al. (2017) [2] indicated that the increasing ratio of FA had a positive effect on the workability of FA based geopolymer concrete. Additionally, it was stated that the increasing curing period time even with low curing temperature enhanced compressive strength, tensile strength, and modulus of elasticity of geopolymers.

This study covers an experimental study to obtain the best design parameters for the production of alkali activated geopolymer material. For this purpose, 6 mixtures were designed with different liquid/material (FA and sand) and alkaline activator ratios (1, 2, and 3). At the end of the curing process, physical tests were determined via bulk density, water absorption tests while mechanical properties were obtained by compressive and flexural tests at the related testing age.

2. Materials and Methods

FA used in this study was obtained from Çatalağzı Thermal Power Plant in Zonguldak (FA). Table 1 presents the physical and chemical properties of FA.

| Compounds        | Amount (%) |
|------------------|------------|
| CaO              | 1.77       |
| SiO$_2$          | 42.12      |
| Al$_2$O$_3$      | 20.27      |
| Fe$_2$O$_3$      | 6.07       |
| MgO              | 1.44       |
| K$_2$O           | 3.81       |
| Na$_2$O          | 0.26       |
| Others           |            |
| Loss on ignition (LOI) (%) | 1.52 |
| Specific gravity | 2.04       |
| BET ($m^2/g$)    | 1.11       |
As seen Table 1, FA can be classified as class F type according to ASTM C618 (2000)[17]. A special sand called as Rilem Cembureau (specific gravity: 2.56, density: 1.35 kg/dm$^3$) (TSE EN 196-1) [18] was used as fine aggregate. The alkaline activator was comprised of Na$_2$SiO$_3$ solution (Na$_2$O=14.7%, SiO$_2$=29.4% and H$_2$O=55.9) and 12M NaOH solution. In the first step, two different alkaline solution/material ratio (FA+standard sand) (L/M) were determined as 0.20 and 0.40, respectively. And then, Na$_2$SiO$_3$ with NaOH in ratio of 1, 2, and 3 by weight were used for the design of geopolymer mortars, respectively. After producing the geopolymer mortar, the samples were cured at 70°C for 24 hrs. The details of mix design of the geopolymer mortar are given Table 2. The test batches were produced until obtaining the slump flow diameter in 16±2 cm.

In the preparing of geopolymer mixture, first of all, Na$_2$SiO$_3$ and NaOH were mixed to get the determined ratio for the alkaline solution (Na$_2$SiO$_3$/NaOH) into the mixer. Then, FA and sand were added to the mixer and mixedtured slowly for 5 minutes to achieve the homogeneity. The mixed mortar was poured into pre-prepared molds with the dimensions of 40x40x160 mm. Finally, the prepared geopolymer samples were placed in a laboratory oven for thermal curing at 70 °C for 24 hours. The mixtures given in Table 2 were coded based on the testing parameters such as the ratio of L/M, the ratio of Na$_2$SiO$_3$/NaOH. For example, if the L/M ratio and Na$_2$SiO$_3$/NaOH ratio were used as 0.2 and 1, respectively, this geopolymer mortars were denoted as 20FA-1.

Table 2. Geopolymer sample mixture properties.

| FA (g) | Sand (g) | Alkaline Activator/Materials Ratio | Na$_2$SiO$_3$/NaOH Ratio (mL/mL) | Testing Temperatures (°C) |
|--------|----------|----------------------------------|---------------------------------|--------------------------|
| 400    | 800      | 1/1                              | 120/120 80/160 60/180          | 70                       |
| 20%    |          | 1/2                              | 80/160              60/180      |                          |
|        |          | 1/3                              | 60/180              40%         |                          |

While the physical properties of the samples were measured by the bulk density and water absorption tests according to ASTM C642-13 (2013) [19] at 28 days, mechanical properties were tested via the compressive and flexural strength tests conducted by ASTM C 348-14 (2017) [20] and ASTM C 349-14 (2017) [21] at 90 days, respectively. The average of six measurements for each test is reported.

3. Results and Discussion
As seen in Figure 1, the bulk density values of geopolymer samples changed between 1842 and 1944 kg/m$^3$. The bulk density of hardened mortars was increased by the ratios of L/M. However, the highest bulk density values were obtained at the ratio of Na$_2$SiO$_3$/NaOH=2. This may be attributed to the change in homogeneity of the geopolymer matrix by the presence of fine sand [22].
Figure 1. Bulk density of geopolymer mortars.

Figure 2. Water absorption capacity of geopolymer mixtures.

Figure 2 indicates that the water absorption values of geopolymer mortars measured at 28 days with different design parameters. The lowest water absorption capacity of geopolymer samples produced at 70 °C curing temperature was found as 10.73% for 20FA-3 while 40FA-1 had the highest one.
(22.87%). As seen in Figure 2, the increasing ratio of L/M resulted in an increment of water absorption capacity for the geopolymer mortars.

Compressive and flexural test results of mixtures are given in Figures 3 and 4 at 90 days, respectively. Despite the increasing of L/M ratio, excessive amount of fine sand gave a reverse effect for the characteristic properties of geopolymer. At 90 days, the lowest compressive and flexural strength values of geopolymer samples were 8.1 and 3.2 MPa for 40FA-1 while 20FA-2 had the highest values found as 36.5 and 8.7 for compressive and flexural test results, respectively.

Increasing of Na₂SiO₃/NaOH solution ratio up to 2 improved the reaction rate and lead to a less porous structures in geopolymer matrix. It may therefore result lower water absorption capacity, thus increases strength for the FA-based geopolymer [13, 23]. The reaction kinetics and the rate of crystallization were affected by the presence of soluble silica. Additionally, the higher percentages of soluble silica in geopolymer affected the dissolution of FA, thus promote the precipitation of larger molecular species, creating in a stronger Si rich gel formation which is responsible for strength development of the material with an enhanced density [13, 24]. But, as seen in Figures 3-4, there was an optimum limit for the Na₂SiO₃/NaOH solution ratio, such that exceeding this limit resulted the adverse conclusion for the strength characteristics of the geopolymer [25, 26].

![Graph showing compressive strength of geopolymer mixtures](image-url)

**Figure 3.** Compressive strength of geopolymer mixtures.
4. Conclusions

Based on the findings of the study, the following conclusions can be drawn:

- Producing geopolymer mortars with L/M ratio of 0.4 resulted in adverse effect for the water absorption, compressive and flexural strength of geopolymer when compared to the ones generated with lower one due to the excessive amount of fine sand.
- Increasing the ratio of Na$_2$SiO$_3$/NaOH gave an increment of strength characteristics up to an optimum point obtained as 2.
- Production of FA-based geopolymer not only provides an opportunity to use FA as a sustainable green material by alkaline activation but also avoids the disposal problems of FA. Additionally, this study contributes the sustainable development technology by decreasing CO$_2$ emissions into the atmosphere since it is a cement-free technology. Thus, geopolymers manufactured in this study with the desired strength characteristic can be used building bricks blocks, tiles, prefabricated materials as well as the infrastructure works.

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