Influence of Alkaline ratios on strength properties of Fly ash- Ground Granulated Blast Furnace Slag Based Geopolymer Mortars

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Abstract: Geopolymer concrete is a new and alternative to cement concrete, thus decreasing greenhouse emissions and leading to better construction practices. This can be produced by complete replacement of cement with pozzolanic materials such as Fly Ash (FA), Ground Granulated Blast Furnace Slag (GGBS) and activation through alkaline activator solution. The present study aims to investigate the effect of 8M sodium hydroxide solution for the chemical ratios of Na\textsubscript{2}SiO\textsubscript{3} to NaOH are 1.5, 2.0, 2.5, and 3 with different combinations of fly ash and GGBS. The cast specimens were outdoor cured and tested at the age of 1, 3, 7, and 28 days for compressive strength, followed by XRD analysis to identify the mineralogical variations with a change in parameters. The obtained results concluded that GGBS content with 8M concentration of sodium hydroxide in the mix increases the compressive strength of geopolymer mortar. The optimum dosage of Na\textsubscript{2}SiO\textsubscript{3}/NaOH was 2.5 based on the compressive strength of mortar. The compounds responsible for strength were identified through XRD analysis as N-A-S-H gel and C-A-S-H gel in mixes with fly ash and GGBS as binders.

Keywords: Compressive strength, Outdoor curing, Polymerization, geopolymer mortar, X-Ray Diffraction analysis.

1. Introduction

Enormous quantities of by-products are generated due to industrial activities, which affect the atmosphere harmfully. A massive amount of carbon dioxide (CO\textsubscript{2}) is emitted during the production processes of cement, which are energy-intensive [1]. Geopolymer (GP) binder is an alternative to the Ordinary Portland Cement (OPC) binder, which is produced by activation the industrialized by-products rich in aluminosilicates like Fly Ash (FA), Ground Granulated Blast Furnace Slag (GGBS), zeolite, etc. with activator liquid [2]. Worldwide several studies have been done on FA-GGBS blended GP binders. FA (Class-F) based binders typically need high curing temperature and high alkali-activator levels to enhance the properties. These alkali liquids are accountable for the higher emissions of carbon dioxide, and manufacturing expenses of GP, as using greater alkali content leads to an improvement in both of these [3]. On the other hand, FA-GGBS based binders require relatively lower activator dosages, which can reduce both issues like CO\textsubscript{2} emissions and cost. Combination FA and GGBS allow ambivalent curing to enable a compact and denser microstructure; as a result, enhanced mechanical properties [4]. Despite around 35-40 years of research studies [5], comparatively few reports concentrated on the optimistic mix proportions in terms of source materials and their influence on the amount of alkaline liquid, fresh and...
hardened properties and recognition of the microstructural products. The majority of the reports available on pastes [6,7] and only some of the investigations are focused on the applications of FA-GGBS based mortar and concretes [8–10]. The significant outcomes from these literature reports were that the replacement of GGBS enhanced the mechanical properties but reduced the consistency and workability. Considering the structure of GP can assist in designing of more reliable and durable constructions [11]. The activator liquid plays an essential role in attaining the strength of GP materials. The solution activates SiO2 and Al2O3 in FA to form N-A-S-H gel and C-A-S-H gel by reacting with calcium in GGBS [12,13].

On the other hand, GPs are formed by treating aluminosilicate materials (such as FA, GGBS, etc.) with alkali liquids. Normally, FA consists of a homogeneous mix of alumina-silicate and quantities of crystalline products like quartz, mullite, magnetite, and hematite [14]. In the formation of GPs, with the combination of FA contributes reactive species through dissolution in the alkaline environment with different Na2SiO3/NaOH, the residue is characterized using X-ray analysis [15].

In this study, an attempt has been made to prepare GP mortars with FA and GGBS, and hardened properties such as compressive strength were determined. Mineralogical variations were studied through XRD analysis. To estimate the effect of alkaline ratios, the mass ratio of Na2SiO3/NaOH solution was varied as 1.5, 2, 2.5, and 3.0. The molarity of sodium hydroxide used in this study was 8M. All the specimens were outdoor cured.

2. Materials

FA and GGBS were used according to ASTM C 618 [16] and ASTM C989 [17], respectively, as binders in the present experimental work. Locally available FA and GGBS were used and mineral composition was shown in Fig. 1. Oxide components of FA and GGBS were presented in Table 1. The local river sand was used as fine aggregate conforming to Zone-II as per BIS: 383-1970 [18] and the specific gravity was 2.64.

![Fig.1. X-Ray Diffraction of binders](image)

| Oxide  | SiO2 | Al₂O₃ | Fe₂O₃ | SO₃  | CaO | MgO | Na₂O | LOI |
|--------|------|-------|-------|------|-----|-----|------|-----|
| Fly ash| 60.11| 26.53 | 4.25  | 0.35 | 4.00| 1.25| 0.22 | 0.88|
| GGBS   | 34.06| 20    | 0.8   | 0.9  | 32.6| 7.89|-     |-    |
2.1. Preparation of Alkaline Solution

The alkaline liquid used in the present experimental work was a blend of NaOH and Na2SiO3 liquids. However, the activation can be done using a NaOH or Na2SiO3 liquid alone, but the reaction process is slower in such a case. The molarity of the NaOH plays a vital role in attaining the strength of the GP samples. The molarity of NaOH is taken as 8M in the experimental program. For the preparation of the NaOH liquid of 8M, 320 grams (8x40) of NaOH pellets were dissolved in one litre of potable water. The prepared NaOH liquid was allowed to cool, and then the NaOH liquid was blended with Na2SiO3 liquid, and the ratios of Na2SiO3/NaOH were varied as 1.5, 2, 2.5, and 3.

2.2. Mixed Proportion

Five mixes were used in this paper with different proportions of FA-GGBS. The ratio of Na2SiO3/NaOH was varied as 1.5, 2.0, 2.5, and 3.0. The density of GP samples was around 2000-2200 kg/m3. The mix proportioning of all the materials were presented in Table 2.

Table 2: Mix Proportions of geopolymer Mortar for different ratios of Na2SiO3/NaOH

| Mix ID | Label   | FA  | GGBS | Fine Aggregate | NaOH | Na2SiO3 | Alkaline liquid | Na2SiO3/NaOH |
|--------|---------|-----|------|----------------|------|---------|----------------|--------------|
| M1     | F100G0  | 880 | 0    | 880            | 176  | 264     | 440            | 1.5          |
| M2     | F75G25  | 660 | 220  | 880            | 176  | 264     | 440            | 1.5          |
| M3     | F50G50  | 440 | 440  | 880            | 176  | 264     | 440            | 1.5          |
| M4     | F25G75  | 220 | 660  | 880            | 176  | 264     | 440            | 1.5          |
| M5     | F0G100  | 0   | 880  | 880            | 176  | 264     | 440            | 1.5          |
| M6     | F100G0  | 880 | 0    | 880            | 146.66 | 293.32 | 440             | 2            |
| M7     | F75G25  | 660 | 220  | 880            | 146.66 | 293.32 | 440             | 2            |
| M8     | F50G50  | 440 | 440  | 880            | 146.66 | 293.32 | 440             | 2            |
| M9     | F25G75  | 220 | 660  | 880            | 146.66 | 293.32 | 440             | 2            |
| M10    | F0G100  | 0   | 880  | 880            | 146.66 | 293.32 | 440             | 2            |
| M11    | F100G0  | 880 | 0    | 880            | 125.7 | 314.28 | 440             | 2.5          |
| M12    | F75G25  | 660 | 220  | 880            | 125.7 | 314.28 | 440             | 2.5          |
| M13    | F50G50  | 440 | 440  | 880            | 125.7 | 314.28 | 440             | 2.5          |
| M14    | F25G75  | 220 | 660  | 880            | 125.7 | 314.28 | 440             | 2.5          |
| M15    | F0G100  | 0   | 880  | 880            | 125.7 | 314.28 | 440             | 2.5          |
| M16    | F100G0  | 880 | 0    | 880            | 110   | 330     | 440             | 3            |
| M17    | F75G25  | 660 | 220  | 880            | 110   | 330     | 440             | 3            |
| M18    | F50G50  | 440 | 440  | 880            | 110   | 330     | 440             | 3            |
| M19    | F25G75  | 220 | 660  | 880            | 110   | 330     | 440             | 3            |
| M20    | F0G100  | 0   | 880  | 880            | 110   | 330     | 440             | 3            |
2.3. Casting and Curing
The binders and fine aggregates were mixed uniformly for 2-3 min in a pan mixer. Next, the activator solution was added and continued blending for another 3-4 min. Consequently, fresh GP mortar placed in the moulds and placed in a vibration table for 1-2 min to remove the air voids. After 24 hours, all the samples were demoulded and placed in outdoor curing for different ages. Fig. 2 illustrates the outdoor curing process of GP mortar samples.

![Fig.2. Geopolymer samples left for Outdoor Curing](image_url)

3. Results and Discussions
3.1 Compressive Strength
The compressive strength of GP mortars with dissimilar proportions of FA and GGBS were considered in the experimental study. The strength of mortar cubes prepared with dissimilar ratios of Na₂SiO₃ to NaOH ranged from 1.1 MPa to 71.78 MPa for all the combinations of FA and GGBS. This clearly shows the effect of activator combinations on the compressive strength of FA and GGBS based GP mortars. The specimen prepared with F100-G0 has deficient strength compared with all other mix combinations of FA and GGBS. With an increase in the GGBS levels, the compressive strength of GP was also enhanced. The early strength was attained with greater percentages of GGBS. The mixture of NaOH to Na₂SiO₃ liquid plays an essential role in gaining the strength. With an increase in the Na₂SiO₃/NaOH ratio from 1.5 to 2.5, the compressive strength increases, and beyond 2.5, the compressive strength decreases. The mineralogical variation and the minerals which are responsible for the strength contribution for all mixes of FA and GGBS were observed through XRD analysis.

The effect of calcium content present in the different combinations of FA and GGBS was studied in the experimental program. In the FA based mixes, the silica and alumina are the main minerals which are responsible for the strength contribution. The dissolution of these minerals helps in attaining the strength through the polymerization process. With the addition of GGBS level in the mix helps in achieving more strength compared with FA based samples. A combination with F100-G0 attained very less strength compared to all the mixes due to less calcium content. The highest Ca/Si ratio was observed in F0-G100 compared with the mixes shows the higher compressive strength, which was observed from Figs. 3-6. The presence of more amounts of Ca results in additional C-A-S-H gel formations, it leads to enhancement of strength. The attainment of the strength in GP mortar mainly depends on the GGBS content in the mix.

The chemical composition present in the source materials and their combinations is responsible for the strength contribution of GP mortars. The replacement of silica and alumina with some amount of calcium...
content is helpful for the formation of the new reaction products like albite, microcline, and anorthite observed through XRD analysis. These minerals are other forms of the alkali aluminosilicate GP gel (N-A-S-H) and calcium alumina silicate hydrate gel. These minerals are responsible for the strength attainments of the GP mortars prepared with dissimilar proportions of FA and GGBS.

![Fig. 3. Compressive Strength of Geopolymer Mortar with Na$_2$SiO$_3$/NaOH -1.5](image1)

![Fig. 4. Compressive Strength of Geopolymer Mortar with Na$_2$SiO$_3$/NaOH -2](image2)
3.1.1. Effect of Age:
The compressive strength of GP mortar specimens prepared with the mix of FA and GGBS increases with an increase in the age of the mortar cubes. At the period of 1 and 3 days, the strength of the mortars was very less when the specimens were compared with 7 and 28 days. The strength increment was observed for the samples prepared with more amount of GGBS content. The maximum strength among all the samples was observed for the mix of F0-G100 at the age of 28 days. The ratio of Na$_2$SiO$_3$ to NaOH plays a crucial role in attaining the strength of GP mortars. The strength was lower for the mixes prepared with sodium silicate to sodium hydroxide ratio 1.5. As the ratio of Na$_2$SiO$_3$ to NaOH increases the strength of the blends with dissimilar proportions of FA and GGBS also increases up to 2.5. After that, the strength decreases due to the large quantity of sodium silicate solution, which will affect the polymerization.
process. Age plays an essential role in influencing the polymerization process, and as the age increases, the strength increases with the formation of C-A-S-H gel.

3.2. XRD analysis

The fragments of mortar cubes after the experiment were ground to a fine powder and were used for XRD analysis. The major reaction products formed during the activation are alumina-silicate products in an amorphous state or poorly crystalline state. The XRD patterns of mortar samples for different combinations of FA and GGBS for different alkali ratios are shown in Fig. 7. The minerals identified in XRD analysis are Quartz (SiO$_2$), Mullite (Al$_2$O$_3$) and Calcite (CaO), Hematite (Fe$_2$O$_3$), Alumina (Al$_2$O$_3$), Alite (Ca$_3$SiO$_5$), Belite (Ca$_2$SiO$_4$) and Portlandite (Ca(OH)$_2$) were observed in all the samples irrespective of mix proportions. Fig. 7 was evident that the main peak detected as quartz at $2\theta = 24.5^\circ$ having N-A-S-H/C-A-S-H, and calcite as associate peaks.

As seen from Fig. 7, the reaction products in mix 100FA-0GGBS were N-A-S-H gel. With an increase in GGBS content, the calcium content increases and results in an increased amount of C-A-S-H gel. It is reported in the literature that the Ca$^{2+}$ ions replace all the Na$^+$ ions in the mix in favor of C-A-S-H formation until available Ca$^{2+}$ is exhausted [19]. The increase in compressive strength at higher dosages of GGBS is due to the structure of C-A-S-H and C-S-H gel along with N-A-S-H gel, which improved the strength of mortar.

The use of higher alkaline ratios increases the silica content resulting in a greater quantity of aluminosilicate gel, which on reaction with available Na$^+$ or Ca$^{2+}$ results in N-A-S-H or C-A-S-H gels. The presence of higher amounts of silicates reacts among themselves, forming oligomeric silicates, which on reaction with alumina results in poly (sialate-siloxo) or poly (sialate-disiloxo) polymer structures. These polymer structures are comparatively more durable than poly (sialate) structures; thereby the strength is improved at higher alkaline ratios. The main reaction product for F100-G0 is N-A-S-H gel, and whereas in F0-G100, the main reaction product was C-A-S-H gel.

For different combinations of FA and GGBS, the peak of C-A-S-H was observed at $2\theta = 24.5^\circ$ approximately. The C-A-S-H was formed due to the polymerization of FA and GGBS with alkali activators, which also has led to the transformation of the amorphous phase to the crystalline phase. The quartz and calcite were the main minerals that are responsible for the strength contribution for the samples prepared with F0-G100 content along with N-A-S-H gel. The strength was much improved for F0-G100 samples and this strength was contributed by the mineral anorthite which was observed through XRD analysis and amorphous compounds dissolve easier than crystalline compounds during the first step of polymerization, yielding greater amounts of reactive SiO$_2$ and Al$_2$O$_3$ to combine during the geopolymeric reaction product, which is responsible for the higher strengths [20].
Fig. 7. XRD analysis of GPC (a) M1-M5, (b) M6-M10, (c) M11-M15, (d) M16-M20

Calculations

This paper presents the effect of Na$_2$SiO$_3$ to NaOH ratios (1.5, 2, 2.5, and 3) on strength properties of geopolymer concrete with different proportions of fly ash and GGBS. From the experimental data the following conclusions were drawn,

- Compressive strength of geopolymer mortar increases with increase in percentage replacement of fly ash with GGBS.
- To develop geopolymer concrete under outdoor curing condition, combination of fly ash with GGBS is a relevant solution.
- The Ca/Si ratio plays an important role in affecting the strength of the geopolymer mortar as there increase in Ca/Si ratio the strength of the geopolymer mortar also increases.
- For the combinations of fly ash and GGBS, the minerals quartz and calcite were responsible for improving the compressive strength of fly ash and GGBS based geopolymer mortars.
- Presence of CaO has a positive effect on strength of mortar due to formation of additional C-A-S-H gel along with N-A-S-H gel.
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