Acid resistance behaviour of Binary blended Geo-polymer Mortar

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Abstract. An investigation on the impact of blended combination using Ground granulated blast furnace slag (GGBS) and Metakaolin (MK) in geopolymer mortar was carried out and presented. The geopolymer is a new generation green binding material and it has replacing total cement usage. Sodium silicate and sodium hydroxide were utilized as alkaline activator solutions for the development of geopolymer mortar and maintain the ratio between the solutions as 2. The sodium hydroxide solution molarity was maintain as 8M. The GGBS was replaced with MK from 0% to 100% with the increment level of 20%. The strength and acid resistance behaviour of blended geopolymer mortar were investigated under ambient curing condition. The results obtained from this investigation indicated that the 60% replacement of GGBS by MK produced higher compressive strength and lesser absorption behaviour in addition to the higher resistance to the acid attack.

1. Introduction

Geopolymer has been considered as an alternate binding material to the conventional cement binder which are prepared by using alkaline activated solution with rich alumino-silicates mineral admixtures [1]. The industrial by-products like Fly-ash (FA), GGBS, MK, Rice husk ash, Silica fume are normally considered for making geopolymer mortar and concrete [1, 2]. Geo-polymerization process takes place when alkali activator solution has been allowed to react with alumino-silicate source materials. The geo-polymerization process developed influenced on source materials, type of activator and temperature condition [2, 3]. The complex process of chemical reaction between the fine powder particles of SiO\textsubscript{2} or SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} compositions with alkaline activator solution develops a cementitious hardened matrix with superior properties than the traditional Portland cement binders [4, 5]. Geo-polymerization is a process by converting amorphous state silica and alumina rich solids to semi-crystalline alumino silicate inorganic polymer or geopolymer [6]. The inorganic reaction products are followed by the condensation of a highly amorphous and cross-linked network, based on SiO\textsubscript{4} and AlO\textsubscript{4} units [4]. Geopolymer is a three dimensional alumino-silicate polymer and it is resemble to zeolites [2, 3].

Fly-ash was extensively utilised for developing the geopolymer binders [7, 8]. Curtin University of Technology was conducted wide-ranging research works on geopolymer concrete using fly-ash [9]. The higher strength of the geopolymer product were obtained when blended source material utilized instead of single material [10]. Heat curing was normally employed to promote the polymerization [11]. The hardened process of Geopolymer concrete was carried out by heating at a temperature
between 60°C to 90°C [12]. Higher compressive strength of geopolymer concrete by activating FA was attained with NaOH at thermal curing between 80°C to 90°C with in a day. At higher temperature environment, polymerisation is quicker and consider to be difficulty for on-site concrete applications [12]. But the thermal cutting has technical restriction of cast-in-situ structural part and attempts have been made by researcher to develop the geopolymer at ambient conditions. Nath and Sarker (2014) reported that the results obtained from FA and GGBS blended geopolymer concrete cured in normal temperature condition were resemblance to conventional concrete. The heat produced during hydration of CaO present in GGBS contributed to accelerate the geo-polymerisation process and develop higher strength development during initial stage [13]. The compressive strength of geopolymer materials governed by the chemical compositions of ingredient employed and rest time [14]. Kumaravel (2014) also found that thermal curing specimens had superior performance than that of normal rested specimen and the right temperature for thermal curing was established at 60°C for 24 hours [15]. Under these theoretical background, this study has been made an attempt to impact on the durability properties of GGBS and MK blended geopolymer mortar cured at atmospheric temperature condition.

2. Materials used
2.1 Binding materials
GGBS and MK were used as source materials for developing the geopolymer mortar. GGBS and MK were purchased from local chemical supplier. Both the binders were kept in sundried condition before blending and thoroughly mixed to achieve homogenous binder. The mixture was retained in an oven for 24 h at 100°C to 110°C before use. The physical properties and chemical compositions of both GGBS and MK are presented in Tables 1 and 2 respectively.

Table 1. Physical properties of GGBS and MK

| Physical Properties   | GGBS  | MK   |
|-----------------------|-------|------|
| Specific gravity      | 2.62  | 2.56 |
| Fineness (m²/kg) (*)  | 395   | 15,000* |
| Bulk density (kg/m³)  | 1100  | 846  |

Table 2. Chemical composition of GGBS and MK

| Chemical Composition | GGBS | MK |
|----------------------|------|----|
| SiO₂                 | 35.43| 53.67 |
| Al₂O₃                | 13.46| 41.71 |
| CaO                  | 40.52| 0.56 |
| Fe₂O₃                | 0.37 | 0.89 |
| MgO                  | 8.69 | 0.01 |
| LOI                  | 0.88 | 0.33 |

2.2. Fine Aggregate
M-sand was employed instead of river sand as fine aggregate. The selected M-sand was obtained from the local artificial sand plant. The specific gravity of M-Sand was found as 2.69. The fineness modulus of M-sand was determined as 2. 76 and it was found as confirming Zone II of IS 383-1970 [16].

2.3. Alkaline Solution
A mixer of sodium silicate (SS) and hydroxide (SH) solutions was used and the ratio between SS to SH was maintained as 2. Both the solutions were obtained from the chemical supplier and the samples are shown in Fig.1 and Fig.2 respectively. The sodium hydroxide was purchased in flakes with 98% purity and it was dissolved in distilled water in order to prepare the solution. The molarity of SH was carefully chosen as 8M. The mixture of alkaline solution was prepared 24 prior to the casting of geopolymer mortar.
3. Experimental program

GGBS and MK were selected to develop the binder with six different combinations by changing replacement level from 0% to 100% with the increment of 20%. The various mix combinations are mentioned in Table 3. The source material to M-sand ratio was retained as 1:3 and the alkaline solution to source material ratio was reserved as 0.5. The ratio between the alkaline solutions (SS/SH) was fixed as 2. A pan mixer was used to prepare the mortar mixes as shown in Figure 3. The mortar cubes of 70.6 mm size were casted for finding the compressive strength and acid resistance performance as shown in Figure 4. The compressive strength development of geopolymer mortar was determined after the rest periods of 3, 7 and 28 days as per IS: 4031 (Part-6)-1988 [17].

![Fig. 1 Sodium Hydroxide flake](image1) ![Fig. 2 Sodium Silicate](image2)

The geopolymer mortar cubes were cured under an atmospheric temperature condition with 63% humidity condition. The durability related acid resistance tests were conducted by using 28 days rested mortar cube specimens. The water absorption and acid resistant tests were conducted to evaluate the durability performance of geopolymer mortar. The water absorption test was conducted using oven dried specimens at a temperature of 85°C for 24 hours [18]. The dried specimens were kept in water for 24 hours and the saturated weight of specimen was determined to find the water absorption level. The hydrochloric acid with 5% concentration was used to test the chemical attack and the concentration of solutions were maintained regularly for 32 weeks by changing periodically. The compressive strength of mortar cubes were determined after 2, 4, 8, 16 and 32 weeks of immersion and strength deterioration factor (SDF) were calculated by using the equation [19]

\[
SDF = \frac{f_{28} - f_a}{f_a}
\]

Where, \(f_{28}\) = Strength of 28 days rested geopolymer mortar
\(f_a\) = Strength of geopolymer mortar after immersed in acidic environment.

| Mix Designation | GGBS (kg/m³) | MK (kg/m³) | M-sand (kg/m³) | Sodium silicate (kg/m³) | Sodium hydroxide (kg/m³) |
|-----------------|--------------|------------|----------------|------------------------|-------------------------|
| G100M0          | 100          | 562.5      | 0              | 1687.5                 | 187                     | 93                      |
| G80M20          | 80           | 450        | 20             | 112.5                  | 1687.5                  | 187                     | 93                      |
| G60M40          | 60           | 337.5      | 40             | 225                    | 1687.5                  | 187                     | 93                      |
| G40M60          | 40           | 225        | 60             | 112.5                  | 1687.5                  | 187                     | 93                      |
| G20M80          | 20           | 112.5      | 80             | 450                    | 1687.5                  | 187                     | 93                      |
| G0M100          | 0            | 0          | 100            | 562.5                  | 1687.5                  | 187                     | 93                      |

4. Results and discussion

4.1 Compressive strength

The compressive strength development of GGBS and MK blended geopolymer with liquid to source material ratio of 0.5 under normal temperature is shown in Fig. 5. The alumino-silicate composition of
GGBS and MK undergoes polymerization during activation in the presence of alkali solution. MK is rich in alumino-silicate composition than GGBS, whereas a reasonable percentage of CaO is present in GGBS. Though the alumino-silicate composition is relatively less for polymerization process in GGBS, the hydration of CaO with presence of water undergoes along with polymerization in geopolymer mortar. The rate of strength development during the initial period was found in higher order due to quick initial polymerization process. The presence of higher SiO$_2$ composition in MK has gained relatively higher strength than that of GGBS in geopolymer mortar. The compressive strength of 3 days cured 100% GGBS and 100% MK geopolymer mortar were determined as 13.35 MPa and 15.39 MPa respectively, whereas, the compressive strength of 28 days cured 100% GGBS and 100% MK geopolymer mortar were found as 43.49 MPa and 46.32 MPa. The insignificant reduction in strength in all the curing period of GGBS geopolymer mortar was found as result of slow leaching of GGBS at the normal temperature.

In order to utilize the benefits of rich alumino-silicate composition of MK, the replacement of GGBS by MK at 20%, 40%, 60% and 80% by weight was initiated to develop the blended binder of geopolymer mortar. The impact of blended binder on strength development of geopolymer mortar was shown in Fig.5. From Fig.5, it was found that the mix G40M60 (40%GGBS + 60%MK) had shown the best performance in strength development of geopolymer mortar. The presence of ample reactive alumino-silicates presence in GGBS and MK combinations can easily dissolves in alkaline solution and enhances polymerization process [20,21]. In addition, the availability of CaO in GGBS supplement the strength due to the formation of hydration products such as C-S-H and C-A-S-H gel which binds the unreacted particles. In order to supplement the best performance combination of GGBS and MK in the blended binder, the relationship between the compressive strength of 28 days cured geopolymer mortar and the percentage of MK has been developed with second order polynomial expression as shown in Fig.6. The empirical relationship was found as $f_c = -0.0047(M)^2 + 0.5064(M) + 42.81$ with the higher correlation coefficient of 0.9788, where $f_c$ is the compressive strength of geopolymer mortar and M is the percentage of MK.
4.2 Water absorption
The water absorption behaviour of geopolymer mortar specimens with respect to rest period are presented in Fig. 7. The water absorption of 3 days cured 100% GGBS and 100% MK geopolymer mortar were determined as 13.17% and 12.67% respectively, whereas, the water absorption of 28 days cured 100% GGBS and 100% MK geopolymer mortar were found 8.75% and 8.38% respectively. After the development of binary blended system in geopolymer mortar with GGBS and MK, the water absorption nature of the geopolymer was decreased and the results highlighted lower absorption in geopolymer mortar in G40M60 mix compared to other binary blended combinations as shown in Fig.7 and found that more than 20% reduction in water absorption in mix G40M60 than G100M0 mix geopolymer mortar. This is due to the reduction of diffusion coefficient of geopolymer mortar due to the formation of crystalline compound with the presence of SiO\textsubscript{2} and hydration products with the presence of CaO compound in GGBS [18, 22]. The correlation between the compressive strength of 28 days cured geopolymer mortar and the water absorption in all the curing periods considered in this investigation was developed and is shown in Fig.8. A perfect linear relationship was established and found the empirical relationship as $f_c = -7.1109 w + 105.28$ with the higher correlation coefficient of 0.9617, where $f_c$ is the compressive strength of geopolymer mortar and $w$ is the water absorption of corresponding geopolymer mortar.
4.3 Acid resistance
SDF results of geopolymer mortar specimens exposed in acidic solution up to 32 weeks are presented in Fig. 9. It can be observed that the minor loss of compressive strength in the early immersion period (up to 8 weeks). Though the insignificant strength reduction was observed during initial immersion period, there was no significant visual sign noticed. Initially, the strength reduction due to immersion of specimens in the $5\% \text{H}_2\text{SO}_4$ after 2 weeks was measured and found the SDF in the range of $3.02\%$ to $4.94\%$. The higher percentage was noticed in G100M0 mix specimens and the lower percentage was observation in G40M60 mix specimen. The G100M0 samples were affected due to acid attack during the initial period relatively higher amount when compared to other mixes considered in this investigation and found the SDF as $15.64\%$ and $19.08\%$ at the end of 4 weeks and 8 weeks respectively. This is due to the presence of an equal amount of calcium content in GGBS when compared to silica as chemical compound. The formation of ettringite due to the CaO causes more deterioration of mortar however the development of blended geopolymer with MK reduces this problem due to negligible amount of CaO presence in MK. The lowest rate of strength reduction was noticed in G40M60 mix specimens and had shown $7.98\%$ strength loss after 32 weeks. Dhavamani Doss [18] found the strength reduction of geopolymer concrete after the specimens immersed in
sulphuric acid solution as 17.5% for an immersion period of 2 months and compared this result with cement concrete with the results of 82%. However the strength gain was noticed after 8 weeks immersion period and the fluctuation in the SDF was observed due to the extension of polymerization and formation of new zeolite phase which reduce the porosity of geopolymer mortar [8, 9]. The third order polynomial correlation between the immersion period in weeks and SDF were developed in order to understand the fluctuations in SDF and shown in Fig. 9. The equations of correlation in various mixes and its coefficient were mentioned in Table 3. With the aid of results obtained, the rich silica composites built geopolymer mortar has higher resistance to the acid attack.

Table 3. Correlation between SDF and immersion period in acid solution

| Mix ID | Equations of correlation | R² |
|--------|--------------------------|----|
| G100M0 | y = 0.0075x³ - 0.3954x² + 5.697x - 3.6705 | 0.9417 |
| G80M20 | y = 0.005x³ - 0.2619x² + 3.7965x - 1.4055 | 0.9666 |
| G60M40 | y = 0.0036x³ - 0.1868x² + 2.7083x - 1.1143 | 0.9728 |
| G40M60 | y = 0.0029x³ - 0.1495x² + 2.0775x - 0.5019 | 0.9788 |
| G20M80 | y = 0.0046x³ - 0.2419x² + 3.5176x - 2.0695 | 0.9882 |
| G0M100 | y = 0.0061x³ - 0.3174x² + 4.5147x - 2.4731 | 0.9736 |

Figure 9. Strength deterioration factor of geopolymer mortar

5. Conclusions
The salient point of this research were highlighted below:

- The strength development of geopolymer mortar resembles to Portland cement mortar when it was cured in atmospheric temperature.
- The presence of abundant reactive alumino-silicates in the GGBS and MK combinations that can quickly melts in alkali activator solution and enhances the polymerization process and also the existence of CaO in GGBS supplements the strength due to the development of hydration products.
- The water absorption of the geopolymer mortar with blended source materials combination was decreased due to the formation of crystalline compound with the presence of SiO₂ and hydration products with the presence of CaO compound in GGBS.
- The resistance against acid attack was increased due to the formation of dense mortar with the aid of early geo-polymerisation leads to reduce the SDF significantly.

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