Effect of ratio between Na$_2$SiO$_3$ and NaOH solutions and curing temperature on the early age properties of geopolymer mortar

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Abstract. Geopolymer is the new generation civil engineering material and it is replacing the conventional cement in constructional activities. Sodium silicate (Na$_2$SiO$_3$) and sodium hydroxide (NaOH) solutions were used as alkaline activators to develop the geopolymer mortar in this investigation. The effect of the ratio of Na$_2$SiO$_3$ / NaOH (SS/SH) in the activator solution on the fresh and hardened mortar strength were studied and reported in this paper. Thermal curing was followed in most of the previous research findings and it has various limitations for cast-in-situ applications. Further, the ambient temperature curing method was considered in this study to overcome the limitations and the results were compared and presented. The control geopolymer mortar was developed with class F type fly-ash (FA). Ground granulated blast furnace slag (GGBS) and corn cob ash (CCA) were substituted as FA replacing basic materials. The experimental results had shown that the addition of GGBS and CCA reduced the flow value and setting time of fresh geopolymer mortar and increasing the compressive strength of geopolymer mortar. The experimental outcomes showed that the compressive strength of geopolymer mortar was increased due to increasing the ratio SS/SH. While considering ambient curing environment instead of thermal curing, the strength development pattern was modified and compressive strength was decreased in all the rest period.

1. Introduction

Geopolymer mortar is a potential futuristic alternate binder to Portland cement mortar. The geopolymer material is an inorganic product which is produced from alumino-silicate materials [1]. The industrial by-products from various sources such as GGBS, FA, silica fume (SF), and rice husk ash (RHA) are the few examples of alumino-silicate materials. Polymerization is the reaction mechanism which depends up on the chemical composition of such source materials and the alkaline solution utilized for making the geopolymer products [2]. The curing temperature condition is another important criteria and the polymerization mechanism is accelerated at high temperature condition [3]. The thermal curing had been utilized effectively for prefabricated small size elements and the fabrication of large size prefabricated geopolymer structural elements are having restrictions due to the space limit of heat chamber [4]. The
ambient temperature curing is the possible option for such large size structural elements and cast-in-site construction. Extensive research activities were carried out with FA over the past two decades. The rate of reaction of FA based geopolymer was observed as slower in ambient temperature condition than the thermal curing. The amount of silica present in the FA is readily react with alkaline solution forms alumino-silicate geopolymer gel [5, 6]. In order to increase the early strength properties of FA based geopolymer, blended source materials were utilized by suitable amount of FA replaced by other silica rich source materials like SF, Metakaolin (MK) and GGBS. The SF and FA blended combination and FA and MK combinations were investigated the impact of replacing FA by alternate silica rich source materials [7, 8]. The geopolymer mortar developed with blended source material were reported higher compressive strength than that of made with single source material [9, 10]. The geopolymer mortar developed with bottom ash and RHA blended source material produced better results in ambient temperature curing [11].

The amount of calcium content presents in GGBS was found as higher order than FA and the notable amount of CaO presents in such source material reacted with the presence of water to form C-S-H (gel) along with alumino-silicate polymer product [12]. Several research findings were reported the compatibility between the source material to improve the performance of geopolymer products [13, 14, 15].

In addition the blended combination of source material, the proper selection alkaline combinations are also another important factor for improving the polymerization process. The ratio between the Na₂SiO₃ and NaOH are place a vital role in the selection of alkaline solution combination [16]. However the research finding specified that the SS/SH ratio between 2-2.5 had shown the better results [17]. In this background, the present investigation was focused on the ternary blended source material using GGBS and corn cob ash (CCA) which was developed in our centre. The tests were carried out in thermal curing and ambient temperature curing in order to evaluate the suitability of ambient temperature curing. In addition the impact of ratio between alkaline solutions on the fresh and hardened mortar properties were investigated and reported.

2. Experimental program
2.1 Materials used
Class F type FA, GGBS and CCA were used as the source materials for developing the geopolymer mortar. The FA was collected from NTPC thermal power plant, Ramagundam, Telangana state, India and considered as the main source of alumino-silicate materials. The commercially available GGBS and newly developed CCA [18] were used as a substitute source materials and added 30% and 20% respectively to replace the FA for developing blended additive in this experimental investigation. The physical properties and chemical compositions of additives are shown in Table 1. The alkaline activator was obtained by mixing the sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH) solutions. The market available NaOH was procured in the form of pellets with 97%-98% purity and the NaOH solution was prepared by mixing the pellets with potable water and the concentration of NaOH was maintained (8M) throughout investigation. The commercially available NaSiO₃ with 2M molarity was used. The fine aggregate used was M.sand having the grading limit of zone II and specific gravity of 2.68.

2.2 Sample preparation
The selected quantity of alkaline solutions were mixed together 60 minutes before preparing the geopolymer mortar. The source materials were mixed by a pan mixer for 2 minutes and M-sand was then added in the source material to develop a dry uniform material. Later, the prepared alkaline solution was added gradually and mixing all the ingredients for 5 minutes in order to achieve a homogeneous mixture. The mortar cube specimens were prepared using 7.07 cm size cube mould.
Table 1. Physical properties and Chemical composition of additives

| Chemical Composition (%) | Class F type FA | GGBS | CCA  |
|--------------------------|----------------|------|------|
| SiO₂                     | 54.5           | 35.43| 61.05|
| Al₂O₃                    | 25.6           | 13.46| 9.73 |
| SiO₂ + Al₂O₃             | 80.1           | 48.89| 70.78|
| CaO                      | 3.5            | 40.52| 10.85|
| Fe₂O₃                    | 4.9            | 0.37 | 8.33 |
| MgO                      | 2.7            | 8.69 | 7.68 |
| LOI                      | 2.3            | 0.88 | 1.32 |

| Physical Properties      |                |      |      |
|--------------------------|----------------|------|------|
| Specific gravity         | 2.62           | 2.86 | 2.15 |
| Fineness (m²/kg)         | 395            | 410  | 560  |

2.3 Curing
The high temperature (thermal) curing and ambient temperature curing methods were used to evaluate the effect of curing methods on geopolymer mortar with varying the alkaline solution ratio.

2.3.1 Thermal curing
The specimens were de-moulded after 24 hours of casting and were kept in oven at 90°C for about 8 hours (72 degree hour) for thermal curing. In order to avoid the sudden variation of temperature condition, the specimens were allowed to cool up to room temperature condition in the oven itself. Then the compressive strength of specimen were tested after the rest period of 3, 7, 14, 28 and 56 days.

2.3.2 Ambient temperature curing
After casting the specimens, the moulds were kept in controlled ambient temperature condition and allowed the top face surface wide-open to atmosphere. Mortar cubes were removed from the moulds after a period of 24 hours and were kept in the ambient temperature condition with 65±5% relative humidity up to the testing periods.

2.4 Testing methods
The consistency of the geopolymer mortar was tested with flow test immediately after mixing in accordance with ASTM C1437-07. The final and initial setting time of mortar is in accordance with ASTM C191-08. Both the flow test and setting time tests were conducted at an ambient temperature condition. The compression test was conducted after the rest period of 3, 7, 14, 28 and 56 days. The results mentioned in this study was calculating the mean value of three testing specimen results.

2.5 Mixture proportioning
The mixture proportion of the proposed mortar was developed with 50% FA, 30% GGBS and 20% CCA based on a preliminary laboratory investigation [19]. The control geopolymer mortar mixture (CM) was developed initially with 100% class-F type FA for comparing the results with different mixture considered in this investigation. The investigation was mainly focused on the effect of different ratios between the alkaline solution (Na₂SiO₃ / NaOH) and the effect of curing method. The mixture designation was mentioned accordingly as shown in Table 2. The mixture R-1.5, R-2 and R-2.5 were mentioned as the ratio between the alkaline solutions with 1.5, 2 and 2.5 respectively. The mixture proportions were designed by considering the unit weight of mortar as 2200 kg/m³. The total source material was maintained as constant with one fourth of all ingredients.
Table 2. Mixture proportioning of geopolymer mortar

| Mixture designation | M.sand | FA | GGBS | Corncob ash | SS | SH |
|---------------------|--------|----|------|-------------|----|----|
| CM                  | 1350   | 550| 0    | 0           | 180| 120|
| R-1.5               | 1350   | 275| 165  | 110         | 180| 120|
| R-2                 | 1350   | 275| 165  | 110         | 200| 100|
| R-2.5               | 1350   | 275| 165  | 110         | 214.3| 85.7|

3. Results and discussion

3.1 Effect of Na$_2$SiO$_3$ / NaOH ratio on the flow value of geopolymer mortar

The influence of ratio between Na$_2$SiO$_3$ and NaOH on the flow value of fresh geopolymer mortar depicts in Fig.1. The consistency of geopolymer mortar was affected due to the variation of the ratio between the alkaline solutions. The sodium silicate solution is highly viscous when compared to the sodium hydroxide solution. The higher ratio between SS/SH increases the viscosity and restrict the flow of geopolymer mortar [20]. The flow value of R-1.5 mix geopolymer mortar was determined as 91% which is 27% lower than the CM mixture. Higher the FA content had shown higher the flow value due to the particle shape of the FA particles. However the flow values of R-2 and R-2.5 were calculated as 85% and 78% respectively which indicates the reduction of flow of mortar while increasing Na$_2$SiO$_3$ content in the alkaline solution. The flow value of control geopolymer mortar which was developed with FA and SS/SH ratio of 1.5 was found as 103%. The higher flow value was due to the spherical nature of FA particle and the addition of GGBS and CCA as partial replacement restrict the flow nature of geopolymer. It was experimentally noticed that increasing the SS/SH ratio along with reduction of FA particles causes the reduction of flow value of geopolymer mortar.

3.2 Effect of Na$_2$SiO$_3$ / NaOH ratio on the setting time of geo-polymer mortar

The differences in final and initial setting time of geo-polymer mortar due to raising the SS / SH relationship is present in Fig.2. The final and initial setting time of R-1.5 geo-polymer mortar was determined as 380 minutes and 610 minutes respectively. However these setting time of control mortar with SS/SH ratio of 1.5 were determined as 425 min. and 670 min. respectively. The reduction of setting time in FA, GGBS and CCA blended geopolymer was observed by the same SS/SH ratio of 1.5, due to the presence of high CaO content in GGBS and also higher SiO$_2$ in CCA which accelerate the reaction during initial period. It was observed from the Fig. 2 that the reducing the final and initial setting time of geo-polymer mortar while raising the SS/SH ratio in the alkaline solution though all additional source materials remains constant. This reduction in results had shown due to the effect of chemical compositions of the alkaline solutions on the setting behaviour of fresh geo-polymer mortar. When raising the SS/SH ratio, the presence of soluble silica in the mixture accelerate the polymerization process resulted the reduction of both final and initial setting time of geo-polymer mortar [21].

3.3 Effect of Na$_2$SiO$_3$ / NaOH ratio on compressive strength of geopolymer mortar

The compressive strength development of geopolymer mortar under thermal curing is shown in Fig.3. The compressive strength of mortar after 3 days of thermal curing was found as 31.33 MPa and it was as found as 34.57 MPa after 28 days of rest period. The substitution of GGBS in the mixture accelerate the polymerization process along with hydration process due to the presence of CaO content with water and hence the early strength development of geopolymer mortar with SS/SH ratio of 1.5 was observed in higher order than the control mortar [22]. The compressive strength of geo-polymer mortar was found raising with higher SS/SH ratio. While increasing SS/SH ratio with the higher amount of Na$_2$SiO$_3$ content
promote the geo-polymerization and rise the compressive strength during the initial period. It was found that more than 90% of 28 days compressive strength was attained within 3 days while the mortar geo-polymer was subjected to thermal curing.

The compressive strength development of geo-polymer mortar under ambient temperature curing is shown in Fig.4. The strength development of CM geo-polymer mortar during early period was significantly low when it was cured under ambient temperature condition. However the GGBS and CCA blended geopolymer mortar had shown slightly higher strength than that of CM specimens in the early period of curing. The variation of SS/SH ratio did not show any significant difference in strength development up to 7 days curing under ambient temperature. Later, internal heat generation during reaction of CaO in GGBS and forming C-A-S-H and C-S-H gel which binds the unreacted particles accelerate the compressive strength of geo-polymer mortar. In addition, the higher dosage of Na$_2$SiO$_3$ while increasing the SS/SH ratio, promote the polymerization process and causes continuous development of compressive strength. The strength development of geo-polymer mortar subjected to ambient temperature curing resembles with Portland cement mortar strength development. The compressive strength of thermal curing specimen had shown nearly 15% higher than the ambient temperature curing after the rest period 28 days. However the 3 days rest period specimens had shown more than 50% higher
while in thermal cured condition than that of ambient cured condition. From the results obtained from the two different curing environment, thermal curing is superior to ambient curing.

![Compressive strength development by thermal curing](image1)

**Figure 3.** Compressive strength development by thermal curing

![Compressive strength development by ambient temperature curing](image2)

**Figure 4.** Compressive strength development by ambient temperature curing

### 4. Conclusions

With the support of this investigation results, the following conclusions were arrived:

- The flow value of R-1.5 mix geopolymer mortar was fund as 91% which is 27% lower than the FA based control mortar. Further reduction of flow value was identified due to increasing the alkaline solution from 1.5 to 2 and 2.5.
- Reduction in final and initial setting time of geo-polymer mortar while increasing the SS/SH ratio in the alkaline solution.
- Compressive strength development of GGBS and CCA blended geopolymer mortar was higher than the FA based control mortar.
The thermal curing mortar cubes had shown higher strength in the early periods rather than the ambient curing geopolymer mortar in all the ratios of alkaline solutions.

The compressive strength development of geo-polymer mortar was insignificantly lower at 28 and 56 days curing, however the strength development of ambient cured mortar cubes are resemblance to the cement mortar strength development pattern.

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