

Study on Fly Ash Based Geopolymer Blended With Calcium at Different Curing Profile

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Abstract : Based on mixing composition, curing conditions, geopolymer shows different performance. The most important parameter in consideration with the synthesis of geopolymer is curing condition. In this research, a relative study between the requirement of curing temperature and curing time with the mix combination was studied. Three series of samples were separated into different curing condition such as curing at 35°C, 55°C, 85°C for 1 day and up to 2 days. The workability at green state and compressive strength at harden state were evaluated. Result showed that curing condition has been significantly influenced on the mixing composition. The change in strength with the increase in curing temperature is remarkable for fly ash based geopolymer without any calcium compound as a supplement. Whereas geopolymer specimens blended with calcium compound led to optimized strength even at lower curing temperature. Similarly curing at higher temperature for prolong period is not necessarily required for the sample containing calcium compound as a supplementary material.

Keywords- Geopolymer, Curing Condition, Calcium Compound, Fly ash, Workability, Compressive Strength

I. INTRODUCTION

The clear reaction mechanism of geopolymer is not available. As per the earlier research, proposed mechanism consists of a dissolution, orientation and poly condensation [1]. The waste materials like fly ash, lime stone dust contain sufficient amount of reacting alumina and silica that can be used as base material for geopolymerization. The mix composition, raw material, processing typically influence the characteristics like compressive strength, shrinkage, setting, durability, thermal conductivity and also the adhesiveness at green level [2-9]. Various parameters like water content,

alkali percentage, silicate modulus and most importantly blending of supplementary material have a substantial effect on the properties of geopolymer [10]. The delay in polymer formation due to higher concentration of activator is omitted and the rate of reaction is accelerated with temperature. The effect of curing temperature on the development of better geopolymer has already been established [11]. Again increment in compressive strength with increase curing time and temperature has been reported by earlier studies [12]. The composition and temperature on the properties of fly ash based geopolymer has a remarkable effect on the compressive strength [13]. Like temperature of curing, the duration of curing affects the synthesis of the mixture, dehydration and shrinkage [14].

The optimization of curing temperature and duration, considering compressive strength for various mixes of fly ash based geopolymer have been discussed. Therefore, this paper represents the optimization of strength with respect to curing temperature and time for various mixes.

II. EXPERIMENTAL

A. Materials

Class F fly ash used in the research was collected from Kolaghat Thermal Power Plant near Kolkata, India. About 75% of particles were finer than 45 micron and Blaine's specific surface was 380m²/kg. The chemical composition of fly ash is given in Table 1. The Limestone dust was brought from BCC Limited, Dhanbad, Jharkhand, India. The Lime stone dust is a solid composite having specific gravity 2.7, bulk density 1425 kg/m³. It has an average particle size of 25 micron while particle size varies between ranges of 10µ to 70µ. The chemical analysis report of Lime stone dust is provided in Table 2. Scanning electron micrographs of fly ash and Lime stone dust is given in Fig. 1 and Fig. 2.

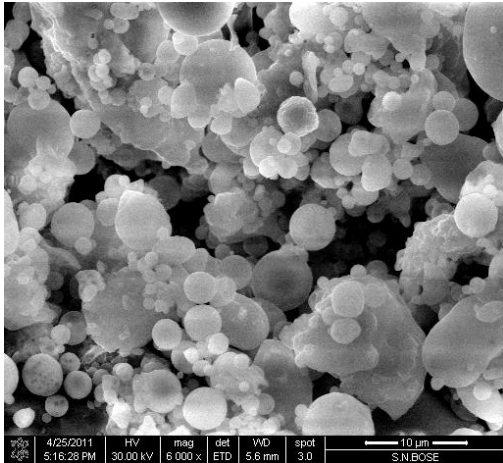


Fig. 1 SEM of Fly ash at 6000x zoom

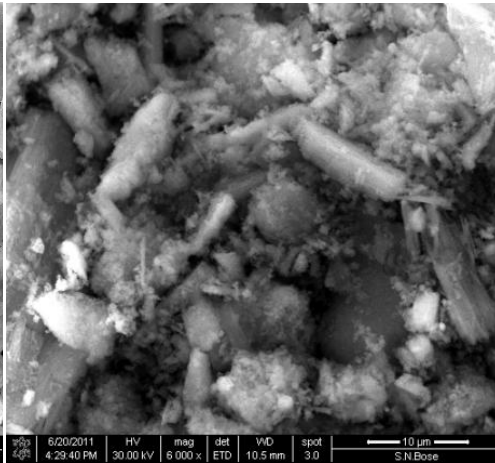


Fig. 2 SEM of Lime stone dust at 6000x zoom

Laboratory grade sodium hydroxide in pellet form (98% purity) and sodium silicate solution (Na₂O= 8%, SiO₂ =26.5% and 65.5% water) with silicate

modulus ~ 3.3 and a bulk density of 1410 kg/m³ was supplied by Loba Chemie Ltd, India.

TABLE 1 CHEMICAL PROPERTIES OF FLY ASH

| Chemical Composition | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | TiO ₂ | CaO | MgO | K ₂ O | Na ₂ O | SO ₃ | P ₂ O ₅ | Loss on Ignition |
|----------------------|------------------|--------------------------------|--------------------------------|------------------|-------|-------|------------------|-------------------|-----------------|-------------------------------|------------------|
| Fly ash | 56.01% | 29.8% | 3.58% | 1.75% | 2.36% | 0.30% | 0.73% | 0.61% | Nil | 0.44% | 0.40% |

TABLE 2 CHEMICAL ANALYSIS REPORT OF LIME STONE

| Chemical Composition | CaO | MgO | Fe ₂ O ₃ | K ₂ O | Na ₂ O | TiO ₂ | Al ₂ O ₃ | SiO ₂ | Loss on Ignition |
|----------------------|--------|-------|--------------------------------|------------------|-------------------|------------------|--------------------------------|------------------|------------------|
| Lime Stone Dust | 51.01% | 0.28% | 0.36% | 0.04% | Nil | 0.09 | 2.74% | 3.92% | 41.56% |

B. Preparation of Solution, Specimens and Testing

By dissolving required quantity of sodium hydroxide pellets directly into water the alkaline activating solution was prepared. The activator solution (sodium hydroxide and water) was left at room temperature for 24 hours after that predetermined quantity of sodium silicatesolution was added 3 hours before casting of geopolymer specimens. It had Na₂O content and SiO₂ content as 8.0% of fly ash, thereby making SiO₂/Na₂O ratio of 1. Water to Fly ash ratio was of 0.33.

In a Hobart mixer, fly ash, with or without lime stone dust (according to Table 3) was mixed with predetermined quantity of activator solution for 5 minutes. The geopolymers were of different consistency as exhibited under a typical workability setup. The mix was transferred into 50 x 50 x 50 mm cubes followed by table vibration for 2 minutes to drive out any entrapped air. After 1 hour of air dry, the cubes were cured in a hot air oven and then allowed to cool inside the oven. Before testing, specimens were removed and stored at ambient temperature in a dry place. Geopolymer paste mixture composition and curing environment is given in Table 3.

TABLE 3 Composition of Different Geopolymer specimen

| Mix ID | Sample ID | Na ₂ O content in activator (% of (fly ash + lime stone dust) in wt. | SiO ₂ content in activator (% of (fly ash + lime stone dust) in wt. | Lime stone dust (%) of (fly ash + lime stone dust) in wt. | Type of specimen | Water / fly ash ratio | Curing temp. | Curing duration |
|--------|-----------|---|--|---|------------------|-----------------------|-------------------|-----------------|
| GP1 | GP1-LS | 8 | 8 | 0 | Paste | 0.33 | 35 ⁰ C | 24 hrs |
| | GP1-LL | 8 | 8 | 0 | Paste | 0.33 | 35 ⁰ C | 48 hrs |
| | GP1-MS | 8 | 8 | 0 | Paste | 0.33 | 55 ⁰ C | 24 hrs |
| | GP1-ML | 8 | 8 | 0 | Paste | 0.33 | 55 ⁰ C | 48 hrs |
| | GP1-HS | 8 | 8 | 0 | Paste | 0.33 | 85 ⁰ C | 24 hrs |
| | GP1-HL | 8 | 8 | 0 | Paste | 0.33 | 85 ⁰ C | 48 hrs |
| GL1 | GL1-LS | 8 | 8 | 10 | Paste | 0.33 | 35 ⁰ C | 24 hrs |
| | GL1-LL | 8 | 8 | 10 | Paste | 0.33 | 35 ⁰ C | 48 hrs |
| | GL1-MS | 8 | 8 | 10 | Paste | 0.33 | 55 ⁰ C | 24 hrs |
| | GL1-ML | 8 | 8 | 10 | Paste | 0.33 | 55 ⁰ C | 48 hrs |
| | GL1-HS | 8 | 8 | 10 | Paste | 0.33 | 85 ⁰ C | 24 hrs |
| | GL1-HL | 8 | 8 | 10 | Paste | 0.33 | 85 ⁰ C | 48 hrs |
| GL2 | GL2-LS | 8 | 8 | 15 | Paste | 0.33 | 35 ⁰ C | 24 hrs |
| | GL2-LL | 8 | 8 | 15 | Paste | 0.33 | 35 ⁰ C | 48 hrs |
| | GL2-MS | 8 | 8 | 15 | Paste | 0.33 | 55 ⁰ C | 24 hrs |
| | GL2-ML | 8 | 8 | 15 | Paste | 0.33 | 55 ⁰ C | 48 hrs |
| | GL2-HS | 8 | 8 | 15 | Paste | 0.33 | 85 ⁰ C | 24 hrs |
| | GL2-HL | 8 | 8 | 15 | Paste | 0.33 | 85 ⁰ C | 48 hrs |

C. Testing and Analysis Method

In the experimental set-up we used a 7mm thick circular glass slab of 50cm diameter to predict the workability. A polar graph was used to study the extent of the spread. The polar graph consists of 50 concentric circles, equally spaced, with the outermost circle having a diameter of 50cm. Each circle was again divided into a number of sectors by 40 number of spokes (i.e., radial lines). This polar graph was placed below the glass slab. It is evident that we can easily determine the area of a small division between two consecutive spokes. As the space between two consecutive circles is 0.5 cm, the diameter of a particular circle is indicated by its number measured from center. Such as the diameter of 50th concentric circle is 50 cm when the diameter for the 1st circle is 1cm. The change of workability corresponding to different mix was assessed by a factor mentioned as Area Factor which is defined by the ratio of final area of the flown geopolymer paste to the initial area i.e. the area of the cylinder.

The compressive strength of the cube specimens were evaluated according to ASTM C109 by using the digital compressive strength testing machine. Every specimen under different curing environment were taken out of oven and put in room temperature for 1 day. The compressive strength was carried out to evaluate the

strength development for the samples. The samples were subjected to compression at 3 days and 28 days of synthesis.

Model quanta 200 mk 2 made in Netherland Scanning Electron Microscopy was used to express the microstructure of geopolymer. In an auto fine coater the scrap of specimens were coated by platinum prior to experiment as shown in Fig. 6.

III. Result and Discussion

A. Workability

Larger presence of calcium emphasizes the faster formation of Ca-Al-Si amorphous structure at the very early stage [15, 16, 17]. Again calcium included compounds like calcium silicates, calcium aluminate hydrates also formed during synthesis of fly ash geo polymer with the presence of calcium [18]. Quick setting behavior was observed for fly ash based geopolymer blended with lime stone dust. The area factor was dropped with the additional lime stone dust. But it is also added the area factor 7.11 is also compatible for placing and shaping.

Table 4 Result of workability test of geopolymer of different mix

| Mix ID | INITIAL DIAMETER (D1) (cm) | FINAL EQUIVALENT DIAMETER (D2) (cm) | INITIAL AREA (A1) (cm ²) | FINAL AREA AFTER FLOW (A2) (cm ²) | AREA FACTOR = A2/A1 |
|--------|----------------------------|-------------------------------------|--------------------------------------|---|---------------------|
| GP1 | 6 | 22 | 28.26 | 379.94 | 13.44 |
| GL1 | 6 | 20 | 28.26 | 314.00 | 11.11 |
| GL2 | 6 | 16 | 28.26 | 200.96 | 7.11 |

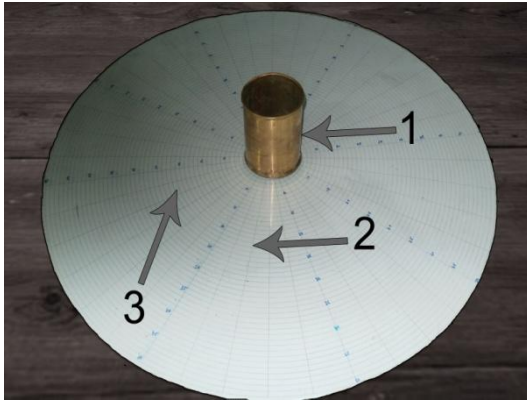


Fig. 3 Worbability Test Setup

1. Cylindrical Brass Container
2. Polar Graph
3. Circular Glass Slab



Fig. 4 Sample GL2 under testing

B. Compressive Strength

The fly ash based geopolymer blended with calcium compound like lime stone dust need less time for geopolymerization due to higher rate of reactivity. On the other hand the fly ash based geopolymer without external calcium sources need sufficient time for geopolymerization process to occur. The non-blended sample did not harden after even 12 hours whereas the blended sample hardened within 2-3 hours for every case.

Again the result indicates that the blended sample cured at 35°C exhibits measurable strength. For the blended sample the difference of strength is not so remarkable when it is subjected to a curing temperature within a range of 55°C to 85°C. The non-blended fly ash based geopolymer led a better strength gain at 85°C whether the value is

remarkably low at 55°C. The compressive strength of non-blended sample cured at 35°C shows zero value.

Higher curing temperature and longer curing duration affects the blended geopolymer structure due to excessive loss of water molecules and corresponding shrinkage.

Curing at moderate temperature 55°C-75°C seems to be best for geopolymer blended with external calcium.

For non-blended geopolymer higher temperature contributed to higher strength gain as it favored the dissolution of reactive species [19].

The effect of aging has almost little to no effect on calcium blended fly ash based geopolymer. But aging has noticeable effect on the strength of non-blended fly ash based geopolymer.

Table 5: Compressive Strength of typical samples

| Mix ID | Sample ID | Curing temp. | Curing duration | Compressive Strength (MPa) | |
|--------|-----------|-------------------|-----------------|----------------------------|---------------|
| | | | | After 3 days | After 28 days |
| GP1 | GP1-LS | 35 ⁰ C | 24 hrs | 0.0 | 0.0 |
| | GP1-LL | 35 ⁰ C | 48 hrs | 3.51 | 4.89 |
| | GP1-MS | 55 ⁰ C | 24 hrs | 9.50 | 10.90 |
| | GP1-ML | 55 ⁰ C | 48 hrs | 13.03 | 18.30 |
| | GP1-HS | 85 ⁰ C | 24 hrs | 28.31 | 35.00 |
| | GP1-HL | 85 ⁰ C | 48 hrs | 37.00 | 44.49 |
| GL1 | GL1-LS | 35 ⁰ C | 24 hrs | 16.16 | 17.09 |
| | GL1-LL | 35 ⁰ C | 48 hrs | 19.70 | 20.00 |
| | GL1-MS | 55 ⁰ C | 24 hrs | 26.00 | 27.90 |
| | GL1-ML | 55 ⁰ C | 48 hrs | 28.57 | 29.34 |
| | GL1-HS | 85 ⁰ C | 24 hrs | 31.89 | 32.00 |
| | GL1-HL | 85 ⁰ C | 48 hrs | 33.21 | 33.50 |
| GL2 | GL2-LS | 35 ⁰ C | 24 hrs | 22.17 | 23.50 |
| | GL2-LL | 35 ⁰ C | 48 hrs | 25.11 | 26.30 |
| | GL2-MS | 55 ⁰ C | 24 hrs | 33.09 | 33.50 |
| | GL2-ML | 55 ⁰ C | 48 hrs | 34.13 | 34.50 |
| | GL2-HS | 85 ⁰ C | 24 hrs | 35.00 | 35.85 |
| | GL2-HL | 85 ⁰ C | 48 hrs | 36.00 | 36.00 |

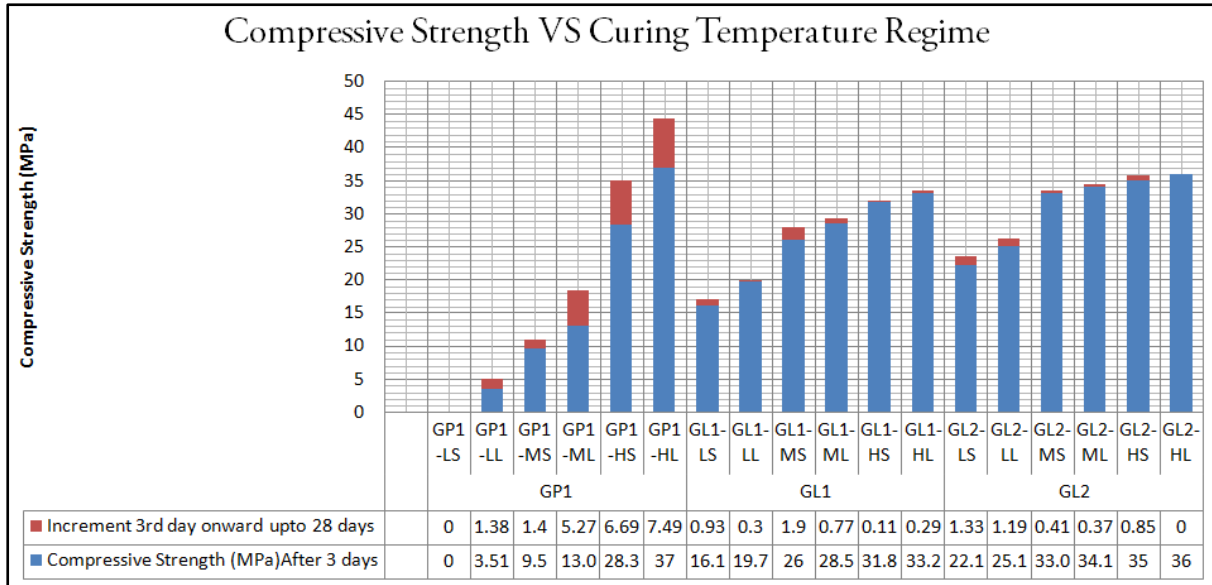


Fig. 5 Compressive Strength VS Curing Temperature Regime

C. Microstructural Analysis

As discussed earlier aging does not disturb the calcium blended geopolymer structure due to which calcium blended geopolymer exhibits little to no change in strength after 3 days. It is also evident that magnitude of strength is not the prime criteria for selecting a good geopolymer structure. Rather, constant strength value is favorable. Parallel to this, an optimized value of strength should be recognized for a construction material. Such as for fly ash based geopolymer blended with 15% lime stone dust gives a compressive strength value 33-34 MPa and 35-36

MPa for a curing temperature domain equal to 55°C and 85°C respectively. This value remains constant even after 100 days. But remarkable fact is that GP1 specimen shows hair crack after 15-16 weeks decades from preparation. Due to which GP1 specimen is accused for this major drawbacks. More than 50% specimens give zero value under compressive load. This phenomenon is due to the progress in the pore pressure within the geopolymer structure. The presence of excessive pore water are predicted by determining the presence of crystalline feature under scanning electron Microscopy as shown in Fig. 7.

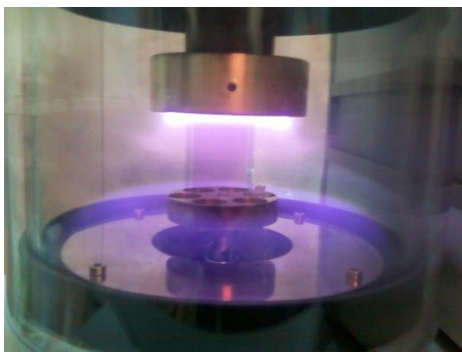


Fig. 6 Coating of sample before SEMFig.

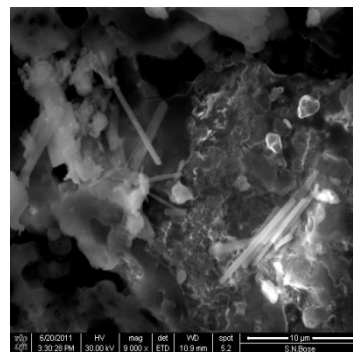


Fig. 7 water crystal in GP1-HL at 9000x zoom

IV. Conclusion

- I. Curing at low temperature is feasible for flyash based geopolymer blended with external calcium compound like lime stone dust. Whereas at a temperature of 35°C the compressive value is zero for flyash based geopolymer without any supplementation.
- II. Presence of additional calcium compound favored the dissolution of reactive species

- III. Curing temperature monitor the primary strength gain for non blended geopolymer.
- IV. The change in compressive strength is very less for blended geopolymer cured at 55°C to 85°C. Only 5.5% increment is observed for GL2 specimen cured at 85°C

over that at 55°C. But compressive strength is observed as three times greater for GP1 specimen cured at 85°C over that at 55°C.

- V. Like curing temperature, the duration of curing has considerable effect on strength gaining for flyash based geopolymer without blending.
- VI. Faster formation of Ca-Al-Si amorphous structure at very early stage brings the quick setting behavior for calcium blended geopolymer sample. Additional lime stone dust is indicted for the drop in area factor in case of sample GL1 and GL2.
- VII. A better stabilized polymeric structure is formed with the addition of external lime stone dust in flyash based geopolymer. The change in compressive strength is almost negligible for this blended geopolymer.
- VIII. Non-blended flyash based geopolymer exhibits the presence of crystal compound (regular shaped structure supporting the presence of water) under scanning electron microscopy. This pore water further increases the internal pressure with time being and create crack in the structure. After 100 days more than 50% specimen of GP1 gives zero value under compression.

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