Development of geopolymer concrete mixes with ambient air curing

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Abstract: Mix design for geopolymer concrete is yet to evolve. Though geopolymer concrete has made the much required transition from laboratory to the field, due to inherent difficulties such as huge variation in the chemical composition of the raw material, the sensitivity of this composition and the chemicals involved in the fresh and hardened properties have led to most of the mix development through trials with the actual materials. The aim of the work reported in this paper was to design an optimum mix proportion for geopolymer concrete using fly ash and ground granulated blast furnace slag (GGBS) as an aluminosilicate source, which has good workability, slump retention, and compressive strength without special curing requirements. A total of 10 mixes were prepared with varying fly ash to GGBS ratios. Ambient curing for 28 days was adopted for all mixes; however, heat curing at 85°C for 24 hours, followed by ambient curing, was adopted for one mix alone. It was clear that with the increase in GGBS content, there was a reduction in setting time, and the mix set faster. However, with more GGBS, greater strength was achieved at a relatively milder alkali activator solution. When the GGBS content increased beyond a certain level, the slump retention time reduced to levels where the mixes were unfit for practical applications. However, it can be concluded that with a judicious choice of fly ash and GGBS proportions, a strength of as high as 60MPa can be achieved in geopolymer concrete without any special curing methods.

1. Introduction
One of the most commonly used construction material worldwide is portland cement. However, its production has resulted in making the cement industry the second-largest producer of greenhouse gases. Each ton of OPC production generates approximately 0.8 tons of carbon dioxide (CO₂). This contributes to 7% of the world's CO₂ emission. Besides, a huge amount of fossil fuel is also consumed to achieve 1400°C for the calcination of limestone. For dealing with this problem, alternatives to OPC are always explored. Portland Pozzolana Cement (PPC) and Portland Slag Cement (PSC) have reduced this problem to a certain extent. But since the fly ash utilization in such cases has been restricted to 35%, still, much of the unused fly ash is an environmental hazard.

“Geopolymer”, an inorganic polymer developed by Prof. J. Davidovits of France in 1978, can be a solution for the safe disposal of fly ash and other similar industrial wastes. Since this geopolymer can be a binder for concrete, it can help reduce the requirement for Portland cement. Geopolymer is an inorganic alumino-silicate polymer. It is synthesized from the polycondensation reaction of
aluminosilicate minerals under the highly alkaline condition that leads to a three-dimensional polymeric chain.

Geopolymer concrete exhibits properties very similar to Portland cement concrete; hence it can be readily accepted in the industry. The rate and the amount of strength development of geopolymer concrete depend on the concentration of the alkaline activator, curing conditions, and the chemical composition of the source material.

It was reported that the partial replacement of fly ash in geopolymer concrete with lime and silica fume up to 7.5 and 2%, respectively, enhanced its compressive strength. Also, properties like setting time and workability reduced with the use of lime and increased with the use of silica fume(1). The value of compressive strength of the geopolymer concrete was reported to be the highest at 28 days when the ratio of alkaline activator to binder was 0.4 and 0.35 for 14M and 12M NaOH concentration, respectively, in the alkaline activator solution(2). Use of 10% of alcalfine by weight of fly ash in geopolymer concrete was observed to give a compressive strength up to 43 MPa(3). The use of only one activating solution (10M NaOH) in an ambient cured geopolymer concrete with 100% GGBS produced a higher compressive strength(4). It was reported that the compressive strength of fly ash based geopolymer concrete, blended with different proportions of GGBS, increased with the increase of the slag content for all ages up to 180 days. But a reduction of activator liquid and the addition of water to improve workability decreased the compressive strength(5). For every 10% increment of the slag content the 28-day compressive strength increased by about 10 MPa. Compressive strength also increased by increasing the Si/Al ratio in the constituents of the mixtures. In contrast, with the increase in alkaline liquid, a reduction of strength occurred while the setting time and workability increased(6). Geopolymer produced using three precursors, consisting of Ground Glass Fiber (GGF), glass-powder and fly ash were compared, and it was observed that while the addition of soluble Si (i.e., increase in SiO₂/Na₂O) to mixtures has improved the compressive strength of glass-powder and fly ash-based geopolymers, it had decreased the compressive strength of GGF geopolymer samples. Samples which had larger Si content showed high early-age strengths and no significant improvement in later ages. It was also observed that GGF samples had the highest compressive strength for all levels of activator dosage on comparing with glass-powder-based geopolymer and fly ash samples(7). Incorporating 10% alcalfine (low calcium silicate slag) while preparing fly ash-based geopolymer concrete, 12M of NaOH solution was found to be of the molarity which was optimal in order to make the GPC more economic(8). It was reported that the geopolymer concrete with ground granulated blast furnace slag (GGBFS) as aluminosilicate source having a binder content of 450 kg/m³, SS/SH ratio of 2.5, SH concentration of 14 M and Alkaline to Binder ratio of 0.35 achieved the highest 7-day compressive strength (60.4 MPa) at ambient curing conditions. However, the setting time was found to be short(9). Fly ash based geopolymer concrete blended with additives like GGBFS (10%) and OPC(8%) showed enhanced compressive strength from the early age of one day. Also, the compressive strength enhanced by increasing the content of the binder from 450 kg/m³ to 730 kg/m³(10). Similar results were also reported when fly ash based geopolymer concrete was prepared with 10% ground blast furnace slag, and with fly ash to slag ratio of 60:40(11, 12). It was reported that the mix containing binder of Fly Ash and GGBS in 40:60 resulted in higher strength, and the ratio of Na₂SiO₃/NaOH of 1.5 resulted in better compressive strength when compared to the other ratio of Na₂SiO₃/NaOH of 2 and 2.5 along with the ratio of Liquid/Binder kept at 0.5(13). The limit of using GGBS was suggested to be at 70% and fly ash to be at 30% for preparation of geopolymer concrete, along with the concentration of NaOH solution at 14M to obtain higher compressive strength(14). It was reported that for the production of sustainable fly ash–slag blended geopolymer mortar (GPM), 25% replacement of fly ash by slag showed the highest compressive strength irrespective of the curing temperature(15). It was also observed that the activator solution when pre-mixed 24 hours before, enhanced the 7- and 28- days compressive strength, despite of negligible changes in the pH(16).
It is evident from the literature available that there is a need to develop an experimental database in order to understand the behaviour of geopolymer concrete from a civil engineering perspective. The majority of the guidelines available on concrete are based on the pool of experimental data. Here, this study would contribute for the same and, in the process, understand the parameters governing the fresh and hardened properties of geopolymer concrete.

2. Experimental Work
Low calcium (Class F) fly ash (FA) used in this study had a specific gravity of 2.2 and a bulk density of 995 Kg/m³ with a fineness (Blaine’s) of 419 (m²/kg). The loss on ignition was around 0.76%. GGBS procured from a commercial source had a specific gravity of 2.9 and a bulk density of 1720 Kg/m³ with a fineness (Blaine’s) of 400 (m²/kg). The loss on ignition was 2.1%. The oxide composition of FA and GGBS obtained from XRF analysis is listed in Table 1. Commercial grade Sodium Hydroxide (SH) flakes and sodium silicate (SS) in liquid form was used. The composition and properties of the SS provided are given in Table 2. River sand used had a specific gravity of 2.68, bulk density of 1685 kg/m³ and fineness modulus of 2.73. Broken angular granite aggregates 20mm downsize with a specific gravity of 2.69, and a bulk density of 1550 kg/m³ was used in making concrete.

| Oxide   | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Na₂O | K₂O | TiO₂ | Mn₂O₃ | SO₃ |
|---------|------|-------|-------|-----|-----|------|-----|------|-------|-----|
| Fly ash | 62.1 | 27.44 | 4.57  | 0.83| 0.55| 0.04 | 1.17| 1.09 | 0.04  | 0.4 |
| GGBS    | 43.4 | 12.5  | -     | 40.3| 1.5 | 0.9  | 0.6 | -    | -     | -   |

Table 1. Oxide Composition of Fly ash and GGBS (%).

| Na₂O (%) | SiO₂ (%) | Total solids (%) | Viscosity (Ns/m²) | Specific gravity |
|----------|----------|------------------|-------------------|------------------|
| 14.20    | 31.20    | 45.40            | 900               | 1.5              |

Table 2. Composition and Properties of Sodium Silicate.

Table 3 gives the details of the mix quantities per cubic meter of concrete. The main parameters in designing the mixes were to achieve a similar slump (about 125mm) and workability with different binder ratios. The quantity and concentration of the alkali activator solution (AAS) were varied accordingly. The AAS adopted here was a combination of sodium hydroxide, sodium silicate, and water. The concentration of the hydroxide varied inversely proportional to the GGBS content in the binder system. It was also attempted to have at least a time of 30 minutes before the mixes started to lose its fluidity.

Preparation of geopolymer concrete involves the preparation of Alkali Activated Solution (AAS) and batching of materials such as FA, GGBS, fine and coarse aggregates. In preparation for AAS solution, the calculated quantity of SH is dissolved in the required quantity of water. Since the dissolution of SH in water is an exothermic reaction leading to a rapid increase in temperature of the solution, mixing is done carefully, and the solution is allowed to reach room temperature before mixing with SS solution. The other materials are weighed, batched and dry mixed in a drum mixer. The required quantity of AAS is gradually added to the dry mix and allowed to mix so as to achieve a homogenous concrete mix. The slump of fresh geopolymer concrete mix is measured, and it is poured into the molds. The cubes were demolded the next day and cured in ambient air for 28 days. Three
cubes of each were tested for compressive strength on the 3rd, 7th, and 28th day from the day of casting. Figure 1 shows a typical slump measurement, and Figure 2 shows the compressive strength determination.

Table 3. Mix Proportion Details.

| Constituents (FA:GGBS) | Mix 1 | Mix 2 | Mix 3 | Mix 4 | Mix 5 | Mix 6 | Mix 6 (H) | Mix 8 | Mix 9 | Mix 10 |
|------------------------|-------|-------|-------|-------|-------|-------|-----------|-------|-------|--------|
| Fly ash                | 0:100 | 20:80 | 40:60 | 50:50 | 60:40 | 80:20 | 80:20     | 50:50 | 50:50 | 0:100  |
| GGBS                   | 400   | 311   | 233   | 200   | 155   | 78    | 78        | 200   | 200   | 300    |
| FA                     | 645   | 645   | 645   | 645   | 645   | 645   | 645       | 645   | 645   | 897    |
| CA                     | 1095  | 1095  | 1095  | 1095  | 1095  | 1095  | 1095      | 1095  | 1095  | 1095   |
| AAS                    | 248   | 257   | 254   | 254   | 252   | 252   | 252       | 248   | 263   | 245    |
| SH (M)                 | 2.5   | 2.5   | 3.5   | 3.8   | 6     | 6     | 5         | 8     | 4     |        |
| SH:SS                  | 01:01.3 | 01:01.3 | 01:01.6 | 01:02 | 01:01.8 | 01:01.5 | 01:02 | 01:02 | 01:02 |

Figure 1. Typical Slump Measurement.  
Figure 2. Typical Compressive Test.

3. Results and discussions

Table 4. Compressive Strength in MPa of the concrete mixes.

| Age       | Mix 1  | Mix 2  | Mix 3  | Mix 4  | Mix 5  | Mix 6  | Mix 6 (H) | Mix 8 | Mix 9 | Mix 10 |
|-----------|--------|--------|--------|--------|--------|--------|-----------|-------|-------|--------|
| 3 days    | 38.34  | 28.24  | 33.67  | 22.6   | 24.5   | 20.9   | 24.22     | 28.35 | 43.5  | 37.45  |
| 7 days    | 54.99  | 33.94  | 38.36  | 24.53  | 28     | 21.71  | 31.35     | 32.6  | 52.5  | 42.8   |
| 28 days   | 67.54  | 68.23  | 45.87  | 36.58  | 30.98  | 23.36  | 44.49     | 52.12 | 58.6  | 49.47  |
Table 5. Molar Ratios.

| Mix | Na₂O/SiO₂ | SiO₂/Al₂O₃ | H₂O/Na₂O | Na₂O/CaO |
|-----|-----------|------------|----------|----------|
| 1   | 0.12      | 6.16       | 33.22    | 0.13     |
| 2   | 0.12      | 5.40       | 34.55    | 0.16     |
| 3   | 0.13      | 4.99       | 26.16    | 0.27     |
| 4   | 0.11      | 4.79       | 29.10    | 0.28     |
| 5   | 0.13      | 4.63       | 24.79    | 0.41     |
| 6   | 0.15      | 4.37       | 17.77    | 1.02     |
| 6(H) | 0.15   | 4.37       | 17.77    | 1.02     |
| 8   | 0.15      | 4.90       | 19.43    | 0.38     |
| 9   | 0.19      | 5.06       | 13.85    | 0.52     |
| 10  | 0.20      | 6.64       | 22.45    | 0.23     |

Table 4 lists the compressive strength developed by the mixes, whereas in Table 5, corresponding molar ratios calculated have been tabulated. Mix 1, which had only GGBS as binder, developed the highest strength. The rate of strength development was also the fastest for this mix. However, the mix began to harden within about 15-20 minutes of stopping the mixing process. Though the initial slump was around the targeted 125mm, since the mix lost fluidity rapidly, it would be very challenging placing the mix in a practical construction scenario. Addition of even 20% fly ash substantially increased the time to the initial hardening process. Mix 2 to Mix 6 had a setting time in the range of 30 – 60 minutes. However, Mix 6 took a very long time to set, about 3 hours. Hence it was decided to try heat curing between the age of 24 hours to 48 hours at 85°C for this mix alone.

Mix 8 and Mix 9 were similar except for the hydroxide concentration. A comparison among them reveals that increasing the concentration of the AAS beyond a point may increase the rate of strength development at the cost of workability, but the final strength gain would not be substantial. Thereby confirming that Strength vs. Concentration of AAS is not a linear relationship, and there exists an optimal point that needs to be determined. Mix 10 is similar to Mix1, however, the binder quantity per cubic meter of concrete was reduced from 400 kg to 300 kg. This resulted in a proportional reduction in strength development. From the oxide ratios, it is clear that Na₂O/SiO₂ and Na₂O/CaO ratios determined the rate of hardening of the mixes. In geopolymer concrete with low calcium fly ash and GGBS, Na₂O/CaO dominates the rate of hardening.

4. Concluding remarks

From the limited experimental studies, the following conclusions can be arrived upon-

i. GGBS helps in achieving higher strength at a lower concentration of AAS.

ii. The setting time of a geopolymer mix is inversely proportional to the Calcium content (GGBS) in the system.

iii. It is recommended to maintain GGBS content of 40-60 percent of total binder content to achieve a balance between strength and workability.

iv. There is no need to adopt a special curing regime such as heat curing or steam curing when the targeted strength in the range of 20-40 MPa. The blending of fly ash and GGBS would be a cost-effective method to achieve this.

v. Further studies revealing parameters connecting geopolymer chemistry with the requirements of concrete technology would be necessary to develop this technology as a practical alternative to Portland cement concrete.
5. References

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Acknowledgment

The authors are highly thankful for the laboratory and administrative support provided by the Council of Scientific and Industrial Research-Structural Engineering Research Centre (CSIR-SERC), Chennai, India.