Micro-level studies of fly ash and GGBS–based geopolymer concrete using SEM and XRD

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In order to recognize the features contributing to strength (geopolymerization) for higher grade of geopolymer concrete, characterization of concrete specimens is needed. Fly Ash (FA) and Ground Granular Blast Furnace Slag (GGBFS) based geopolymer concrete is tested for 28 days’ compressive strength. And the mixes were characterized by adopting various physical-chemical methods such as X-Ray Diffraction analysis (XRD), Scanning Electron Microscope (SEM) This information helps to recognize the contribution of ingredients of mix to strength and resultant properties from the mix in a better way.

Keywords: Fly Ash (FA), Ground Granulated Blast Furnace Slag (GGBS), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM)

1. Introduction
Industrialization is a significant move in any country for its progressing economy. On the contrary, it is an undeniable fact that owing to the expanding industries, there is an adverse effect on the environment and resulted as a challenging issue to be addressed by the countries for the sustainable growth. Predominantly, cement manufacturing industry, plastic industry, dying industry textile mills, thermal power plants etc. are showing detrimental impact on the environment. Cement manufacturing industry alone influencing the heightened the environment pollution ((Husein et al., 2016, Guadas et al., 2016).

2. Materials and methods

2.1 Materials

2.1.1 Fly Ash
Fly ash is a finely powdered waste but a by-product that is produced by steam generating and coal-fired electric plants. It is coal burned material that is comprised of grains of burned fuel. It is collected by electrostatic precipitators or filtration equipment.

2.1.2 Ground Granular Blast Furnace Slag
Ground granulated blast furnace slag (GGBFS) is a by-product from the blast-furnaces used to make iron. These operate at a temperature of about 1500°C and are fed with a carefully controlled mixture of iron-ore, coke and limestone.

2.1.3 Alkaline Solution
The alkaline liquid used was a combination of sodium silicate solution and sodium hydroxide solution. The sodium silicate solution (Na₂O= 13.7%, SiO₂=29.4%, and water=55.9% by mass) was purchased from a local supplier.
2.1.4 Aggregates
As a fine aggregate natural river sand is used. The required relative density in an oven dry condition and the absorption of water by the sand as per IS 2386 (Part III, 1963) are 2.62 and 1% correspondingly. The gradation of the sand is defined by sieve analysis as per IS 383 (1970). Fineness modulus of sand is observed as 2.69. In this investigation the usage of coarse aggregate in crushed granite stones. The sizes of coarse aggregate 20mm and 10mm as per IS 2386 (Part III, 1963) are 2.57 and 0.31% correspondingly.

2.2 Methods

2.2.1 Mix Design

| Materials        | Mix Proportion         | Mix Proportions          |
|------------------|------------------------|--------------------------|
|                  | M45                    | FA0 GGBFS100             | FA25 GGBFS75             | FA50 GGBFS50             |
|                  | weight(kg/cu m.m)      | weight(kg/cu m.m)        | weight(kg/cu m.m)        | weight(kg/cu m.m)        |
|                  | ratio                  | ratio                    | ratio                    | ratio                    |
| Cement           | 553                    | 0.2                      | -                        | -                        |
| Fine aggregate   | 625                    | 0.2                      | 554                      | 0.2                      | 554                      | 0.2                      |
| Coarse aggregate | 606                    | 0.2                      | 776                      | 0.3                      | 776                      | 0.3                      |
|                  | 404                    | 0.1                      | 517                      | 0.2                      | 517                      | 0.2                      |
| Fly ash (class F)| -                      | -                        | 102.2                    | 0.0                      | 204.5                    | 0.0                      |
| GGBFS            | -                      | 0.1                      | 409                      | 0.1                      | 306.7                    | 0.1                      |
| Sodium silicate  | -                      | 102.7                    | 102                      | 102                      | 102                      |
| Sodium hydroxide | -                      | 41                       | 41                       | 41                       |
| Extra water      | -                      | 55                       | 55                       | 55                       |
| Alkaline solution | -                      | 0.35                     | 0.35                     | 0.35                     |
| Water / Geopolymer solids | - | 0.29 | 0.29 | 0.29 |

Mixing proportions
1. Normal concrete – M45
2. FA: GGBS-0.100
3. FA: GGBS-25.75
4. FA: GGBS-50.50

Where FA-Fly Ash
GGBS-Ground Granulated Blast Furnace Slag

2.2.2 Cube compressive strength
Cubes compressive strength for geopolymer concrete is being tested for 28 days. Samples of cube compressive strength after testing are collected randomly. The samples were kept in ambient curing. Dried samples are used for further investigations.
3. Results and discussion

3.1 Compressive strength on cubes

Table 2 shows the compressive strength of cubes.

| Mix               | Cube compressive strength (MPa) |
|-------------------|---------------------------------|
| M45               | 51.39                           |
| FA-0 + GGBS-100%  | 60.23                           |
| FA-25%+GGBS-75%   | 58.12                           |
| FA-50%+GGBFS-50%  | 46.32                           |

3.2 XRD (X-Ray Diffraction)

The CSH phase is the strong peak located at around $2\theta = 30^\circ$. It is one of the main products of alkali-activated slag. The diffractogram for the control concrete and geopolymer concrete are in similar range ($2\theta = 20^\circ$ to $30^\circ$). But the hump range of geopolymer concrete is increased with increase in GGBFS content is observed. For control concrete the CSH formation is in the range of 25 to 30 ($2\theta$) (Gslkin et al., 2018, kovba, 1976) result in denser nature of concrete (Figure 2 (c) and 2 (d)). But for the geopolymer concrete the formation of alkaline aluminosilicate hydrate gel (NASH) which has been identified as the primary reaction product of geopolymerization reaction result in increase in hump of CSH (Figure 1 (c) and 1 (d)). The NASH amorphous gel matrix results from the inter-geopolymerization of the fly ash glassy spheres (Figure 2(a)) with the alkaline solution. The increase of GGBFS in the mixes resulting in the increase of the peak intensity of CSH and NASH (Figure 1 (a) and 1(b)). Table 1 indicates the similar observations from literatures.

3.3 Scanning Electron Microscope (SEM)

GGBFS consists of circular particles (A) and prismatic particles (B) – The clearly visible silica is magnified to 50$\mu$m on the geopolymer concrete surface. The geopolymer binders that are characterized are dense and bulky base gel-like substances. Microcracks and micropores which are gel like are clearly observed on the surface (Figure 1 (a)). Through denser matrix micro cracks are detected. Geopolymer samples exhibit distinguished microstructures with slag content at higher magnification which further forms a denser matrix. The expansion of geopolymer matrix depends on the reactions at the external rim of the particles in geopolymerization method. It further produces reaction products that surround and cement the particles, alternatively dissolution of the particles.

![Figure 1. XRD of Geopolymer Concrete.](image-url)
It can be seen the formation of CSH. The presence of calcium in the GGBFS is validated by the EDS analysis (at around 18 wt%), indicating that the increase in the amount of GGBFS considerably increases the calcium content in the mixture, resulting in the formation of a calcium silicate hydrate (CSH) gel (Figure 2(b)). Thus, the inclusion of GGBFS introduces additional calcium that bears compounds and contributes to additional binding products. This also enhances the compressive strength, reduces porosity and modifies the setting behaviour of geopolymeric gels at early stage. This enables the formation of a more compact gel structure and consequently improves mechanical properties. Presence of fly ash particles (F) in the cement matrix. The fly ash particles react with the GGBFS (G) and fills the gap and start reacting with GGBFS there by enhance the properties. The area of crack initiation in surface of geopolymer concrete is reduced due to presence of fly ash particles (F) (Figure 2(c)). Fly ash particles are clearly observed with porous nature. Disintegration of fly ash particles from the polymerization matrix. Random distribution of fly ash particles is seen in the scale of 40 microns. Fly ash particles are partially reacted and some fully reacted particles are seen randomly in Figure 2(d). Reacted and unreacted fly ash particles are visible in higher magnification is seen. Porous nature also observed clearly visible.

Table 3 XRD for geopolymer from literatures

| 2 theta | Compounds            | Reference                    |
|---------|----------------------|------------------------------|
| 17.94   | CH                   | Portlandite                  |
|         |                      | Galkin et al., 2018          |
| 28.58   | CH                   | Portlandite                  |
|         |                      | Galkin et al., 2018          |
| 34.12   | CH                   | Portlandite                  |
|         |                      | Galkin et al., 2018          |
| 25.64   | CSH                  | Calcium silicate hydrate     |
|         |                      | Galkin et al., 2018          |
|         |                      | Kovba, 1976                  |
|         |                      | Gorshkov et al., 1981        |
| 29.94   | CSH                  | Calcium silicate hydrate     |
|         |                      | Galkin et al., 2018          |
|         |                      | Kovba, 1976                  |
|         |                      | Gorshkov et al., 1981        |
| 30.92   | CSH                  | Calcium silicate hydrate     |
|         |                      | Galkin et al., 2018          |
|         |                      | Kovba, 1976                  |
|         |                      | Gorshkov et al., 1981        |
| 22.82   | CaAlSH$_3$           | Ettringite                   |
|         |                      | Galkin et al., 2018          |
| 34.9    | CaAlSH$_3$           | Ettringite                   |
|         |                      | Galkin et al., 2018          |
| 50      | Quatz                | Silica                       |
Figure 2. SEM images of higher volume of GGBFS.

Presence of fly ash particles in the cracks are observed (Figure 3(a)). The particles size of fly ash is similar to the crack of geopolymer concrete results in enhancing the properties. Fly ash particles are partially reacted and some fully reacted particles are seen frequently in Figure 3 (a). Porous, heterogeneous mixture of non- or partly reacted fly ash grains, residual alkaline precipitates, and geopolymer gel are observed. Crack is growing at the area of accumulation of fly ash particles are clearly visible. Denser than all other concrete is observed in surface. Fly ash particles form week link in matrix result in crack propagation (Figure 3 (b)). Growth of crack is randomly observed in normal grade of concrete. Splitting of particles from surface of concrete is also observed in Figure 3(c). Light density than geopolymer concrete is observed in same scale of magnification is observed in Figure 3 (d).
Figure 3. SEM images of 50% GGBFS + 50% FA and normal concrete.

4. Conclusion

The present study brings in the following observations. In order to apprehend the polymerization of geopolymer which is based on GGBFS and fly ash, a comprehensive physical-chemical characterization has been followed through. Further, XRD results brings in the reaction products of geopolymerization and hydration reactions. In the process of geopolymerization, NASH and CSH formation is observed. Also, the crystallinity range of two products is noted in two different humps. It is also observed that XRD analysis is supported by EDS analysis, thus demonstrating the existence of sodium hydroxide in geopolymer concrete. Further, SEM analysis exhibits the being of low density, gel kind, needle shaped materials that may further help as binder element.

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