Effects of slag and superplasticizers on alkali activated geopolymer paste

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Abstract. Geopolymers are a type of amorphous alumino-silicate product, and can be synthesised by the polycondensation reaction of geopolymeric precursor and alkali polysilicates. The binder is prepared by the alkaline activation of industrial by-product materials like fly ash, slag, metakaolin, rice husk ash, etc. as a source for aluminosilicate. The most commonly used alkaline activator is the combination of sodium hydroxide (NaOH) and sodium silicate (Na2SiO3). Chemical admixtures are indispensable in alkali activated systems owing to its poor fresh properties such as workability, too quick setting etc. In this study, the chemical admixture – alkali activated binder interactions were carried out by using latest generation superplasticizers, such as Polycarboxylic ether admixture (PCE) and Sulphonated naphthalene formaldehyde (SNF). Mini slump test, initial and final setting time tests were conducted in alkali activated slag blended fly ash based geopolymer paste and the test results were analyzed with respect to parameters such as alkali to binder ratio (a/b), proportion of slag in blended geopolymer paste, type and dosage of superplasticizers. The test results indicated that the workability and setting time of alkali activated geopolymer paste enhanced due to the increase in alkali content and the reduction in slag content. Based on the effect of chemical admixtures in geopolymer mix, SNF performed better than PCE admixture with regards to mini slump test for all the mixes; whereas in the case of setting time test, SNF showed better results only for the mix with 100% slag. In the case of slag blended fly ash based geopolymer paste, both PCE and SNF showed similar effects, and also it was observed that, the flow of the paste got enhanced when the dosage of superplasticizers is increased from 0 to 3% by weight of binders.

1. Introduction

The main ingredient in conventional concrete is Ordinary Portland Cement (OPC) which is used to bind all the aggregates together along with water. The use of cement causes environmental pollution and depletes natural resources like limestone reserves. Large quantities of fuels are required for the manufacturing of cement, resulting in significant emissions of carbon dioxide creating global warming issues. As such, an alternative to cement based binder is required and geopolymer is one of the promising alternatives. The concrete manufactured using geopolymer as binder is generally called as
Geopolymer concrete (GPC). French scientist, Joseph Davidovits introduced the term “geopolymer” which represent the mineral polymers resulting from geochemistry. Geopolymers are alumino-silicate polymers synthesized from industrial byproducts such as fly ash, slag, metakaolin etc. Geopolymerisation process involves a chemical reaction between various alumino-silicate oxides with silicates under highly alkaline conditions, results polymeric Si–O–Al–O bonds, which is presented schematically in Figure 1.

$$n(SiO_2,Al_2O_3) + 2nSiO_2 + 4nH_2O + NaOH \rightarrow Na'_+K'_+ + n(OH)_2-Si-O-Al-O-Si-(OH)_3$$
(Si-Al materials) (1)

$$(OH)_2$$
(Geopolymer precursor)

$$n(OH)_2-Si-O-Al-O-Si-(OH)_3 + NaOH \rightarrow (Na'_+,K'_+)-(Si-O-Al-O-Si-O-)+ 4nH_2O$$
(OH)$$
(2)

(Geopolymer backbone)

Figure 1. Schematic representation of geopolymerisation process [1]

The water released from the second reaction (in Figure 1) helps in the formation of geopolymer and from (1) and (2) it is clear that water has no role in the chemical reaction, but just increases the workability of mix during its handling. Geopolymers are also referred as alkali-activated aluminosilicate binders or alkali activated materials (AAM), because it involves the polycondensation reaction of silica and alumina precursors activated with high alkali content to attain the structural strength instead of forming calcium silicate-hydrates (CSHs) as in conventional concrete.

Alkali-activated binders are considered as a promising sustainable future construction materials, and promoted as an environmentally beneficial option as no cement is used. It can be widely used in precast industry as well as in-situ concreting and is considered as an effective replacement for conventional concrete. Alkali-activated binders can be produced by two ways, either as a one part mix system or as a two-part mix system. In one part mix system, only a dry mixture is needed in addition to water and the dry mixture is prepared by mixing a solid alkali-activator with a solid aluminosilicate precursor with or without a calcination step and is demonstrated in Figure 2. The two part mix type is the most commonly used one, in which liquid activator is used to bind the precursor materials. The common precursor materials used are blast furnace slag, coal derived fly ash, calcined clay and natural pozzolans, and alkali-activators used are MOH and $M_2O\cdot rSiO_2$, where M is either Na or K. The alkali-activated binders can be applied on reinforced concrete, plain concrete and precast concrete components including both reinforced and unreinforced elements. Laskar and Talukdar tried to develop ultra-fine blast furnace slag (UGGBS) based geopolymer as concrete repairing materials [2]. They found that the workability of the UGGBS based geopolymer concrete (GPC) has improved owing to the addition of superplasticizer. Polycarboxylate ether (PCE) based SP was found to perform better than sulphonated naphthalene (SN) based SP at all dosage levels. Also it was found that the compressive and bond strength of the mixes improves till the lower level of PE based SP dosage. In the case of mixes with SN based SP, the addition of SP caused monotonous reduction in the compressive and bond strength. Nath and Sarker made a study aimed to achieve fly ash based geopolymer suitable for curing without elevated heat and it was found that ground granulated blast
furnace slag (GGBFS) enhanced the early strength development at ambient condition [3]. Also workability and setting time reduced with the increase of GGBFS and decrease of alkaline liquid.

The development of mechanical strength of GPC is predominantly influenced by some of the variables such as temperature of curing, time of curing, alkaline solution to solid binder ratio, water content, type of alkali, molarity of alkaline hydroxide solution etc. [5-6]. The workability of GPC can be enhanced by the addition of water content, but it adversely affects other properties. Beyond 16 M NaOH concentration, the properties of GPC are reduced due to lower rate of polymerization and the chemical admixture content develops the workability of concrete [7]. GPC has superior durability characteristics than OPC concrete concerning absorption characteristics, chemical resistance and temperature changes [8]. The hardened properties of GPC can be further enriched by the addition of steel fibres and which displays a better performance than conventional concrete of same grade [9].

![Figure 2. One-part geopolymer mix system [4]](image)

The upturn in NaOH concentration improves the resistance to chloride penetration, corrosion of steel reinforcement and the chloride binding capacity in GPC. The hardened properties of GPC were amended by adding cement in it and also the use of 30 minutes resting solution advances the concrete properties. Increasing fly ash content and curing temperature up to 700°C improves the hardened properties of GPC and reduces the absorption properties [10-11]. GPC can be used for structural members and there exists ample possibility of using GPC for large scale constructions [12].

The focal issue faced by the alkali activated concrete is the low workability and poor slump retention, and the chemical admixtures are the finest option to solve this issue without the loss of strength. The commonly used superplasticizers (SP) in AAM are Lignosulphonates (WRRe), Sulphonated melamine formaldehyde (SMF), Sulphonated naphthalene formaldehyde (SNF) and Polycarboxylic ether (PCE). According to Rashad the workability and compressive strength of alkali activated fly ash mix was improved only with the use of WRRe based chemical admixtures, whereas PCE and SMF have negative impact in workability [13]. The dosage of 3.3% PCE based superplasticizers was found to reduce the strength by 54%, while, 1.19% dosage of SNF based SP reduces 21.8% strength [14].

Viscosity can be improved by the addition of SNF but PCE retards the viscosity of paste and also flash set can be induced [15-16]. The optimum dosage of liquid commercial PCE with poly oxy ethylene side chains was 0.2% with regarding to workability and which was faintly more effective than solid PCE (SPC). But in the case of strength results, SPC provide better performance with a dosage of 0.15%. By mini slump test, it was found that the spread ratio increases with increase in dosage of SP, and also improves the rheological parameters. The water reduction of 4.3% was obtained at 0.2% SPC value, and the initial and final setting time enhanced at 0.1% SPC [17]. The compressive strength and degree of reaction enhanced up to 1% dosage of chemical admixtures, and
beyond that limit, i.e., 1-2%, the reduction in the compressive strength and degree of reactions were prominent [18].

In some literatures, it was eminent that, both PCE and SNF type admixtures modified the mix workability, setting time and liquid demand mainly in fly ash dominated AAM. But in GGBFS dominated AAM, the effects of admixtures were not significant. Compared to Portland cement mix, fly ash based AAM required higher dosage of admixtures (≥ 1 to 10%) for achieving the desired flowability and consistency. When PCE is added to AAM, it enhances the microstructure development through the densification of interfacial transition zone between AAM gel and solid particles, and thereby the porosity and permeability reduced and chloride resistance enhanced. The optimum dosage for superplasticizers in concrete mix was found to be 3 kg/m$^3$ (0.75% by weight of binder) with regards to compressive strength and chloride migration [19]. The setting time, workability and strength performance were improved by the addition of PCE admixtures in ultra-fine slag – fly ash based geopolymer only up to a certain dosage level. If the concentration of alkali activators is increased, then the admixtures become ineffective in modifying the fresh and hardened properties. The better performance was obtained with a SP dosage of 1.5% with respect to workability and 0.5% with regards to the strength [20]. In slag based geopolymer, SNF based SP was most effective while in the case of fly ash based geopolymers, PCE was found to be the better one. The variations in reported results may due to the changes in compositions, type and amount of slag and activators, curing process and time, concentration of activator, type and dosage of SP [21]. The effectiveness of chemical admixtures in producing satisfactory alkali activated concrete is still being investigated. Literature study revealed that only very few studies have been conducted in the field of chemical admixture-alkali activated binder interactions. Hence, the behaviour of various alkali activated binder system dosed with different chemical admixtures are to be studied for the commercial propagation of geopolymer, as a viable construction material. Hence, this study focuses on the GPC – chemical admixture interactions so as to obtain a workable mix and also aimed to establish the effects of slag in modifying the fresh properties of fly ash based geopolymer paste.

2. Materials and Methods

2.1 Materials

In this study, the constituent materials used for making geopolymer paste were Class F fly ash, ground granulated blast furnace slag (GGBFS), alkaline solution, and superplasticizers. Low-calcium fly ash conforming to IS: 3812-2010 and GGBFS obtained from Astra Chemicals, Chennai were used for preparing the geopolymer mix. The alkaline solution comprised of a mixture of sodium silicate and sodium hydroxide solution. Sodium silicate solution with SiO$_2$ to Na$_2$O ratio by mass of 2.4 and 40% solid content sodium silicate was used. Density of sodium silicate solution was 1.59 g/cm$^3$ and NaOH pellets with 97-98% purity were mixed with water to make a solution of 10 M concentration. The superplasticizers used in the study were Ceraplast 300 (SNF based) conforming to ASTM C 494 - 98 Type F and IS 9103-1999 and Cerahyperplast XR W40 (PCE based) conforming to the standards, ASTM C 494-03, BS 5075 and IS 9103.

2.2 Mix Proportion and Synthesis

The different mix variables such as amount of GGBFS in replacement of fly ash (0%, 25%, 50%, 75% and 100%), the amounts of alkaline activator solution with respect to mass of solid binder materials, i.e., a/b (0.40, 0.50 and 0.60), the type of SP (PCE and SNF) and dosage of SP (i.e., 0%, 1%, 2% and 3%) were varied in this study. No extra water was added to the mix. For the preparation of 10M NaOH solution, the solid NaOH pellets were mixed with distilled water and allowed to cool in room temperature, and finally the Na$_2$SiO$_3$ solution was added, in which the ratio of Na$_2$SiO$_3$ to NaOH was kept as 2.5 and then properly stirred and provide a rest period of 24 hours beore adding to the mixer. The geopolymer solid binders were mixed with alkaline solutions in a Hobart mixer, and then
superplasticiser were added (to the remaining alkaline solutions) and mixed for three minutes. After proper mixing, the fresh paste prepared was used for conducting mini slump test and setting time test.

2.3 Experiments
The workability of fresh geopolymer paste was tested by mini slump test. In this test, the flowability of geopolymer paste immediately after mixing was evaluated in fastest and easiest way. The freshly prepared paste was poured into the truncated conical mould (Figure 3) with 19 mm top diameter, 38 mm bottom diameter and a height of 57 mm. The mould was placed at the centre of the glass plate, and the top surface was levelled by removing the extra paste. After lifting the mould vertically, the two perpendicular diameters of paste spread were measured and then the average value was taken. From the measured average diameter value (final diameter), the % spread was calculated.

\[
\% \text{ spread} = \frac{\text{Final Diameter} - \text{Initial Diameter}}{\text{Initial Diameter}} \times 100
\]

![Figure 3. Dimensions of Mini-slump cone in mm](image)

Based on the similarities of geopolymers and Portland cements, IS: 4031-Part 5-1988 standard test method for cement was used for evaluating the setting time of geopolymers[22]. This method was based on the time of penetration of Vicat needle, in the freshly prepared slurry. The time taken for the penetration of 5±0.5mm from the bottom was taken as the initial setting time and the time when the annular ring fails to make the impression on the paste was recorded as the final setting time.

3. Results and Discussions

3.1 Workability of fresh geopolymer paste
Mini slump spread of all mixes with various a/b ratios, type and dosage of SP and percentage of slag are shown in Figure 4. The results suggested that flow spread increases with an increase in alkali to binder ratio and the dosage of SP. This is because, as the alkaline solution content increases, more the liquid content, enhancing the workability. The highest flow value of 346.19% was obtained for 100% fly ash geopolymer paste with a/b ratio of 0.60, which was found to be independent of the type and dosage of SP.

Addition of SP enhanced the workability by 18% and SNF based SP displayed better performance when compared to PCE based SP. The similar result value was obtained for the mix with 25% slag incorporated paste, with higher dosage of SNF (3% by weight of binder). The paste mixes without superplasticizers were workable only for higher a/b ratios and fly ash content (Slag content up to 50%). Highly stiff and cohesive geopolymer paste (i.e., flow value less than 120%) was obtained for
low a/b ratio mix (i.e. 0.40) with low dosage of SP (0 and 1%). The test results indicate that as the GGBFS content increases, the flow property decreases. This may be due to higher fineness of slag and angular shape of slag grains. This might have resulted in high water demand and hence as a result, the workability was found to be lesser at higher dosages of slag. Similar observations were made by Arun et al. with regards to workability when slag is incorporated [23].

3.2 Setting time test
The initial setting time of the prepared mixes with admixtures was found to vary from 31 to 499 minutes whereas the final setting times varied from 40 to 515 minutes. The variations in setting times for the various mixes with varying dosages of SP are shown in Figure 5. For 100% slag paste, quick setting occurs, even without the use of superplasticizing admixtures. The maximum value of initial setting time of 499 minute was observed for 3% SNF admixed paste containing 25% slag and 75% fly ash. When the slag content was increased from 25% to 50% for the same mix, the initial setting time was reduced to 178 minute. A significant decrease of setting time is noted with an increase of GGBFS content in FA-GGBFS mix. This tendency clearly indicates that at an ambient temperature, slag rapidly gets activated by alkaline solution in comparison to fly ash (which needs high temperature curing for activation). The release of Ca$^{2+}$ ions is promoted besides the release of Si$^{4+}$ and Al$^{3+}$ ions from the slag particles in the aqueous solution of NaOH. Higher calcium content in slag supports the hydration reaction of slag besides the geopolymerization reaction. These supplementary hydration products along with geopolymeric reaction products decreases the setting times [24].
Figure 4. Effects of slag and SP type on mini slump spread of paste

- **Figure 4a**: Initial setting time (25% slag + 75% fly ash)
- **Figure 4b**: Final setting time (25% slag + 75% fly ash)
4. Conclusions
The effect of inclusion of slag, type and dosage of superplasticizers on the fresh properties of alkali activated fly ash paste was investigated in the study. Fly ash was replaced with slag at 25% increments and the effect of two types of admixtures (SNF and PCE) on paste was also studied. The investigations were carried out by conducting the mini slump test and setting time test on the prepared paste. The main conclusions drawn from the study are as follows:

- Workability and setting time of geopolymer paste can be improved by increasing the alkaline solution to binder ratio. The use of alkali to binder ratio of 0.40 results in a stiff and low workable
mix, and hence not recommended for practical uses. The effects of higher dosage of SP at this low alkali to binder ratios are to be investigated further.

- SNF performs better than PCE with regards to mini slump test for all the mixes and in the case of setting time test, SNF shows more effectiveness in retarding the setting time for the paste with 100% slag. In alkali activated slag blended geopolymer, SNF and PCE have comparable results regarding to setting time test.

- When the dosage of SP increases from 0-3%, the workability also increases irrespective of the type of SP. Workability and setting time were reduced with increase in slag content in slag blended geopolymer paste and the optimum replacement of fly ash with slag can be taken as below 50% in the preparation of geopolymers with ambient curing.

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