Effect of Plasticizer and Superplasticizer on Workability of Fly Ash Based Geopolymer Concrete

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Abstract—An attempt has been made in the present investigation to study variation of workability of fly ash based geopolymer concrete with the variation of lignin based plasticizer and poly-carboxylic ether based superplasticizer. It has been observed that there exists a critical value of molar strength of sodium hydroxide beyond which superplasticizer and plasticizer have adverse effect on workability of fly ash based geopolymer concrete. Below the critical molar strength of sodium hydroxide, there is an increase in slump. Lignin based first generation plasticizer shows better performance in terms of workability over third generation superplasticizer below the critical value of molar strength. It was also observed that there is a good correlation between the rheological parameters and slump for fly ash based geopolymer concrete incorporating plasticizer and superplasticizer.

Keywords—Workability, Superplasticizer, Fly Ash, Geopolymer

I. INTRODUCTION

GEOPOLYMER concrete is a promising field of research recently because it utilizes industrial waste and by-products. Fly ash based geopolymer concrete contains alkali-activated fly ash as binder. Fly ash is readily dissolved in the alkaline solution and lends itself to geo-polymerization. In geopolymer, polymerization takes place yielding Si-O-Al bonds as follows:

\[ M_n [(Si-O)_z-Al-O]_n wH_2O \]

where \( M \) is the alkaline element, the symbol – indicates the presence of a bond, \( z \) is 1, 2 or 3 and \( n \) is the degree of polymerization. The end product is an amorphous polymer. The alkali activation of fly ash and other mineral admixtures is a complex chemical process evolving dissolution of raw materials, transportation or orientation and poly-condensation of the reaction products. Fly ash based geopolymer concrete has shown its environmental performance and superior durability over ordinary Portland cement concrete. The alkali activators normally used in geopolymer are either mixture of sodium hydroxide and sodium silicate or mixture of potassium hydroxide and potassium silicate [Palomo et al (1994), Palomo et al (2004), Hardjito et al (2004)], Zhang (2003), Khale and Chaudhary (2007), Duxson et al (2007) presented review on geopolymer and summarized previous research on geopolymer.

There has been extensive research on geopolymer concrete for strength and durability in recent years and several researcher highlighted potential use of fly ash based geopolymer concrete in concrete industry. Many published literature on fly ash based geopolymer concrete for conventional single-point workability tests are also available. But limited reports on the combined effect of plasticizer/superplasticizer and mix parameters are only available. An attempt has therefore been made in the present paper to study the combined effect of several mix parameters as well as plasticizer and superplasticizer dosage on the workability of fly ash based geopolymer concrete.

II. EXPERIMENTAL INVESTIGATION

A. Mix Proportions

Several geopolymer mixes were prepared with different mix proportions with Class F fly ash, sand and coarse aggregates. The mix proportions and designations are listed in Table 1. In Table 1, \( M \) represents molar strength of NaOH and \( R \) is the ratio of the weight of sodium silicate solution to the weight of sodium hydroxide solution.

B. Fine Aggregate

Locally available river sand (water absorption= 1.5%; moisture content= 0.5%; specific gravity=2.6) was used in the present work. Sieve analysis, specific gravity, moisture content, water absorption was determined as per Indian Standard Code, IS: 2386. The particle size distribution is shown in Table 2.

C. Coarse Aggregate

Graded crushed stone aggregate (water absorption= 0.9%; moisture content= 0.25%; specific gravity=2.6) of maximum size 16 mm was collected and stored in the laboratory. The physical properties were determined as per the code stated above. The particle size distribution is presented in Table 3. Aggregates were not sieved and were used as received directly from the stockpile.

D. Fly Ash

Class F fly ash collected by electrostatic precipitator, obtained from National Thermal Power Corporation at...
Farakka (India) was used in the present study. The specifications of the fly ash conform to the Indian Standard Code of practice IS 3812-1982: Specification for fly ash for use as pozzolana and admixture. The chemical composition of fly ash in the present study is as follows:

Specific gravity = 2.10; Loss on ignition = 0.8%; SiO2 + Fe2O3 + Al2O3 = 89.8%

E. Alkaline Activators

In geopolymer concrete, either mixture of sodium hydroxide and sodium silicate solution or mixture of potassium hydroxide and potassium silicate solution is commonly used. A mixture of sodium hydroxide and sodium silicate solution was chosen in the present study as alkali activators. Sodium based solutions were chosen because they were cheaper and it was reported that NaOH possesses greater capacity to liberate silicate and aluminate monomers [Duxon et al (2007)]. It is also reported that sodium cataions have better zeolitization capabilities in geopolymer forming systems [Duxon et al (2007)]. The Commercial grade sodium hydroxide in pellets (purity 97%; specific gravity 2.13) and sodium silicate solution (Na2O=18.2%, SiO2=36.7%, water=45.1%; specific gravity=1.53) were used to prepare the solution. The mass of NaOH pellets in a solution varied according to molar strength M and the mass of silicate solution was taken according to the ratio R.

F. Water Reducing Admixtures

To study the effect of water reducing admixtures on workability, two types of chemical admixtures viz. lignin based 1st generation water reducer (lignin) and poly-carboxylic ether based 3rd generation high range water reducer (PC) were used. The water reducer’s dosage used in the present study is the weight of water reducer expressed as percentage of fly ash content.

G. Mixing

Concrete was mixed in a tilting mixer (laboratory type). The weight of the materials was taken with a digital weighing balance. Mixing sequence was as follows:

- Prepare requisite quantity of sodium hydroxide and sodium silicate solution 24 hours in advance;
- Mix the solutions of sodium hydroxide and sodium silicate solution;
- Mix coarse aggregate, fine aggregate and fly ash for two minutes;
- Add alkaline solutions and water reducing admixture during mixing and mix for two minutes;
- Stop mixing and pour the concrete mix

III. RESULTS AND DISCUSSION

Dosage of plasticizer/superplasticizer affecting workability of fly ash based geopolymer concrete, and effectiveness of plasticizer/superplasticizer at different molar strengths have been studied and presented in subsequent paragraphs.

Fig 1 presents the variation of slump with the variation of water reducing admixture (WRA) dosage for Mix 1. It may be observed that there is an appreciable increase in slump incorporating both the admixtures namely lignin and PC. The admixtures seem to serve their plasticizing effect by dispersing the particles apart, which in turn improves workability by releasing water trapped in the flocs. It may also be observed that the improvement of workability in the present study is more with lignin based water reducer (1st generation plasticizer) compared to PC based admixture (3rd generation superplasticizer). At lignin dosage 1.5% and above, there was segregation of the mix; the particles constituting the paste separated forming a dense lower phase and a creamy upper phase. The variation of workability in the present study is in contradiction to the works reported by Criado et al (2009), Bakharev et al (2000) and Douglas and Brandster (1990). It is to be mentioned that Criado et al (2009) observed improvement in flow value for fly ash based geopolymer mortar incorporating PC but observed decrease in flow value using lignin based chemical admixture. Bakharev et al (2000), Douglas and Brandster (1990) concluded that presence of naphthalene based admixture (2nd generation superplasticizer) did not improve alkaline system workability. Criado et al (2009) also observed that addition of lignin resulted in segregation of fly ash based geopolymer mortar.

The variation of slump with the variation of plasticizer/superplasticizer dosage for Mix 2 is presented in Fig 2. It may be observed that there is a tremendous decrease in slump after addition of plasticizer/superplasticizer which is just opposite to that shown in Fig 1. As before, lignin based plasticizer shows better performance compared to 3rd generation PC superplasticizer. The probable reason for decrease in slump may be higher molar concentration of NaOH solution compared to Mix 1, though the exact reason is to be investigated further. The slump values at different water reducer dosage were very low after addition of chemical admixtures and the rheological tests were not conducted for Mix 2.

To investigate the probable effect of molar strength of NaOH solution on the effectiveness of plasticizer/superplasticizer, Mix 2 was chosen as reference mix. Slump test was carried out for mixes by changing the molar strength of NaOH for Mix 2. The results are shown in Fig 3. It may be observed that at 4M concentration, the effect of addition of superplasticizer/plasticizer is negligible. Mixes containing NaOH solutions with molar strength above 4 M show decrease in slump whereas there is increase in workability for all mixes with chemical admixtures at molar strength less than 4 M. It may also be observed from Fig 3 that the performance of lignin based plasticizer is still better compared to 3rd generation superplasticizer at all molar strengths of NaOH solution except 1.5 M.

The behavior of fly ash based geopolymer concretes using lignin based plasticizer and PC based superplasticizer are contradictory to the OPC system incorporating these admixtures. In OPC system, PC is much more effective compared to lignin based admixture. It is to be remembered that these admixtures are proven suitable for OPC system and established theories are available for their mode of action. The hydration reaction mechanism of OPC and alkali activation reaction mechanism are totally different; the hydration product
of OPC and reaction product of fly ash based geopolymer concrete are also different. Water reducers including PC are designed to form complexes with the dissolved Ca\(^{2+}\) formed during early phases of OPC hydration. In case of fly ash system, there are no dissolved Ca\(^{2+}\) ions. Therefore, the mode of action by which slump increases or decreases is difficult to explain in context with the present study and needs further investigation. For the same reason, it is not clear why lignin imparts better workability than PC admixtures.

The segregation of fly ash based geopolymer concrete after addition of lignin also needs further study. In a study of activated slag systems, Palacios and Puertas (2004; 2005) reported changes in infra-red spectra of a naphthalene based admixture when stored in a mixture of sodium hydroxide and sodium silicate solution. The changes in spectra were attributed certain changes in sulfonates responsible for plasticizing effect. Lignin based admixture might have experienced similar alterations in the present study and concrete containing lignin suffered from segregation.

### IV. CONCLUSION

The following conclusions may be derived from the present study:

- Plasticizer and superplasticizer dosage improves workability (measured by slump test) of fly ash based geopolymer concrete for molar strength of NaOH solution less than 4 M. As the dose of water reducer increases, there is a decrease in the value of rheological parameters. In general, 1\(^{st}\) generation lignin based water reducer has been found to be more effective than 3\(^{rd}\) generation PC based superplasticizer. However, segregation of concrete takes place with the addition of lignin based water reducer at 1.5% and above.

- At higher molar concentration of NaOH (above 4 M), plasticizer/superplasticizer dosage has the adverse effect on slump and rheological parameters of fly ash geopolymer concrete. Lignin based plasticizer still shows better performance, measured by slump test, than PC based superplasticizer at higher molar concentrations.

### REFERENCES


### Table 1: Sieve analysis of fine aggregate

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