A study on the setting and flow behaviour of alkali activated slag/fly ash composites in ambient condition

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Abstract. Alkali-activated binders (AAB) are considered as a promising sustainable future construction material, and promoted as an environmentally beneficial option when compared to Ordinary Portland Cement (OPC). Portland cement-based concrete is the most used material in the construction industry. In the production of OPC, harmful gasses like CO₂, NO₂, SO₂ and specks of dust are discharged into the atmosphere due to calcination of limestone and combustion of fossil fuel. Hence in the present scenario, it has become an emphatic necessity to replace Ordinary Portland Cement based concrete with AAB based system (geopolymer) which is more sustainable. The characteristics of geopolymer composites are predominantly influenced by some of the variables such as temperature and time of curing, alkaline solution to solid binder ratio, water content, type of alkaline activators used, molarity of alkaline solution, chemical composition of aluminosilicate precursors etc. Although geopolymer systems are good in terms of durability and strength, the main issue faced for its less popularity in the field application is its low workability, poor slump retention and too fast setting.

The aim of this experimental study is to investigate the compatibility between modern generation superplasticizers (SP) and various alkali activated binder systems prepared using industrial wastes and the evaluation on the effect of alkali binder ratio (a/b) on the fresh properties of alkali activated binder (AAB) systems. Considering the practical implications, it is the need of the hour to develop a geopolymer mix setting in ambient condition. This study focuses on setting and flow behaviour of the alkaline activated composites of slag and fly ash in ambient condition only. The slag/fly ash ratios of 100/0, 75/25, 50/50 and 25/75 by mass and alkali-to-binder ratios of 0.4 to 1 with an increment of 0.1 were used for the study. The type of superplasticizer used for the study is Sulphonated Naphthalene Formaldehyde (SNF) with dosages of 0%, 1%, 2% and 3%. The setting time and the flow of the paste were determined using vicat apparatus and mini slump cone respectively. The penetration resistance of the setting paste was also measured using vicat apparatus. The test results revealed that even though the setting time increase marginally with SP dosage, the use of SNF was not much effective in prolonging the setting time of alkali activated pastes. There was tremendous increase in the initial and final setting time for pastes with an increase in a/b ratio.

1. Introduction

Cement manufacturing industry is the second largest producer of green house gases. Cement based concrete is most widely used in construction practices and is a significant contributor to the environmental issues. There is a strong demand for green concrete with better strength properties and durability without a compromise on the rheological characteristics. The alkali activated binder systems which are good in terms of durability and strength, however lacks in better rheological properties [6].
The reduction in a/b ratio helps to increase compressive strength, impermeability and durability simultaneously but causes reduction in workability [5,9]. The use of superplasticizers enhances the workability and rheological properties even at low a/b ratio [13]. The superplasticizers such as Sulphonated Naphthalene Formaldehyde (SNF), Lignosulphonates (WRRe), Sulphonated Melamine Formaldehyde (SMF), and Polycarboxylic Ether (PCE) are the most commonly researched admixtures to be used in Alkali Activated Materials (AAM). But increase in the dosage of superplasticizer is uneconomical, and the mixes with higher a/b ratios but with reasonable strength need to be developed [10].

Geopolymerisation is a chemical reaction between various alumino-silicate oxides with silicates under highly alkaline conditions forming polymeric Si–O–Al–O bonds and it indicates that any Si–Al material could become a source of geopolymerisation [3]. Micro-structural studies done by Nath and Sarker pointed that aluminosilicate (N–Al–S–H) gel was formed in geopolymerisation reaction in the absence of calcium oxides but if the calcium oxide is incorporated in the form of GGBFS or OPC, into fly ash based geopolymer then calcium silicate hydrate (C–S–H) gel is formed along with the geopolymer gel [8]. The formation of C–S–H gel reduces the cost of heat curing in construction sites and can be used to construct self cured geopolymer composites [3]. Previous studies on the effect of alkali content, silicon to aluminium ratio, water content and the amount of superplasticizer on the workability of fly ash based geopolymers show that increasing the alkali content and silica content result in reduced workability [2]. The early strength development of the mortar at ambient condition is enhanced by incorporating GGBFS as precursor [12] whereas the addition of sulphonated naphthalene formaldehyde (SNF) admixtures increases the workability and shrinkage but reduces the compressive strength [1, 11]. So it is necessary to determine an optimum dosage of SP for each of the alkali to binder ratio used. The effect of superplasticizers on the fly ash based geopolymer directly depends on the type of alkali activator and the superplasticizer [15]. Besides superplasticizers, concentration of alkaline solution also has a significant role in the regulation of setting time, workability, and strength properties of the mixes [7]. Increase in the concentration of alkali reduces the setting time and workability of the mixes [8]. Therefore, studies are to be performed to identify an optimum alkali to binder ratio and corresponding SP dosage.

Only limited studies have been carried out in the area of geopolymer – chemical admixture interactions and about the fresh properties of geopolymer concrete (GPC) in ambient curing conditions [14]. Behaviour of AAB systems using different chemical admixtures need to be studied, and the compatibility of admixture are to be explored further. More scientific studies are needed to find a solution for the aforementioned issues. Thus, this study is aimed at studying the fresh properties such as setting and flow behaviour of alkali activated fly ash/ slag pastes developed in ambient air conditions.

2. Materials used

Ultrafine ground granulated blast-furnace slag (GGBFS) obtained from Astrra Chemicals, Chennai and fly ash obtained from a Ready Mix Concrete plant were used as precursor in the preparation of alkali activated geopolymer mixes. The specific gravity of slag and fly ash were 2.90 and 2.21 respectively. Activator solution is prepared by mixing sodium silicate solution and sodium hydroxide (NaOH) solution in the ratio 2.5 by mass. Sodium silicate solution of density 1.59 gm/cm$^3$ with SiO$_2$ to Na$_2$O ratio by mass of 2.4 and 40% solid content was used. NaOH pellets with 97-98% purity were mixed with distilled water to make a solution of 10M concentration. The superplasticizers investigated in the study were Ceraplast 300 which is a Sulphonated Naphthalene Formaldehyde (SNF) based admixture conforming to ASTM C 494 - 98 Type F and IS 9103-1999. The superplasticizer dosages used in the study are expressed as percentage by weight of the total amount of precursor binders used in the mix. The properties of superplasticizers are provided in table 1.
Table 1. Properties of SNF.

| Appearance | Liquid   |
|------------|----------|
| Colour     | Brown    |
| Solid content % | 32.8 |
| Specific gravity | 1.18 |
| pH         | ≥7       |
| Chloride content | Nil |

3. Methodology

In this study, the tests were conducted in geopolymer paste with alkali-to-binder ratios of 0.4 to 1.0 at increments of 0.10. The type of superplasticizer used for the study is Sulphonated Naphthalene Formaldehyde (SNF) with dosages of 0%, 1%, 2% and 3%. The alkali activator systems selected were slag/ fly ash in the ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 by mass. The workability and setting time was tested using mini slump cone and Vicat apparatus respectively. The precursors were mixed with alkaline solution using Hobart mixer. Then the superplasticizers were added (to the part of alkaline solution) with alkaline solution followed by thorough mixing for three minutes. After proper mixing, both the tests were conducted on the paste simultaneously. The workability of fresh geopolymer paste was studied using mini slump cone test apparatus shown in Figure 1. The mini slump cone was 3D printed using nylon.

The mini slump cone test apparatus was placed above the centre of a glass plate. The freshly prepared paste was poured into the mini-slump test setup which is a downscaled Abram’s truncated conical mould having 19 mm top diameter, 38 mm bottom diameter and a height of 57 mm. The extra paste was removed and top surface levelled as shown in Figure 2. After lifting the mould vertically, diameters of paste spread in two perpendicular direction were measured and then the average value was taken as the final diameter of the spread [16]. The % spread was calculated from the measured value of average final diameter based on equation (1).

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

As per IS 4031 Part 5 (2004) [4], Vicat apparatus was used to measure initial and final setting time of the paste. The time of penetration of Vicat needle is taken as basis for the conductance of these tests in the freshly prepared paste. The time taken by initial setting needle to penetrate a distance of
5±0.5mm from the bottom of the mould was taken as the initial setting time and the time when the annular ring of the final setting needle fails to make the impression on the paste was recorded as the final setting time of the paste [4].

4. Results and discussions

4.1. Mini slump cone test

The % spread of paste obtained for different mixes with varying a/b ratios and variation of flow with SP dosages of different mixes are shown in the Figure 3 to Figure 6.

The results (Figure 3 to 6) show that the spread of the paste that increase dramatically in the lower a/b ratio becomes almost constant at higher a/b ratios. Even though the maximum flow values differ, all the mixes were showing similar trend in the flow with an increase in alkali content. Also it was found that flow increases with increase in the fly ash content. The variation in flow with a/b ratio for paste with slag/fly ash 50/50 and without SP is shown in the Table 2. It can be seen that flow increases with an increase in a/b ratio. Table 3 shows the variation in flow of paste with slag/fly ash 100/0 at a constant a/b = 0.40 with an increase in superplasticizer dosage (from 0 to 3%). It is seen that flow increases with SP dosage at a constant a/b ratio. But, high dosage of SP was needed to make the paste flowable.

The variation of flow with SP dosage for each mix is indicated graphically in Figures 7 to 10. The flow was found to be increasing with SP dosages (minimal increase). However, the effectiveness of SP in increasing the flow was found to be lesser when compared to a/b ratio. The mixes with slag/fly ash 100/0, and 25/75 with alkali to binder ratio of 0.40 and SP 2% satisfies the range of workability 110±5% as per IS 4031(Part 7) – 1988.
Table 2. Variation of flow with a/b ratio for paste with slag/fly ash 50/50.

| Mix | Mini Slump Flow |
|-----|-----------------|
| Mix with Slag/ fly ash 50/50, SP dosage = 0 % and a/b = 0.4 | ![Image] |
| Mix with Slag/ fly ash 50/50, SP dosage = 0 % and a/b = 0.5 | ![Image] |
| Mix with Slag/ fly ash 50/50, SP dosage = 0 % and a/b = 0.6 | ![Image] |
| Mix with Slag/ fly ash 50/50, SP dosage = 0 % and a/b = 0.7 | ![Image] |
| Mix with Slag/ fly ash 50/50, SP dosage = 0 % and a/b = 0.8 | ![Image] |
| Mix with Slag/ fly ash 50/50, SP dosage = 0 % and a/b = 0.9 | ![Image] |
Table 3. Variation of flow with SP dosage for paste with slag/fly ash 100/0 at a/b of 0.40.

| Mix | Mini Slump Flow |
|-----|-----------------|
| Slag/fly ash 100/0, a/b = 0.4 and SP dosage = 0 % | ![Image](image1.jpg) |
| Slag/fly ash 100/0, a/b = 0.4 and SP dosage = 1 % | ![Image](image2.jpg) |
| Slag/fly ash 100/0, a/b = 0.4 and SP dosage = 2 % | ![Image](image3.jpg) |
| Slag/fly ash 100/0, a/b = 0.4 and SP dosage = 3 % | ![Image](image4.jpg) |

Figure 7. Variation of flow with SP dosage of mix with Slag/Fly ash 100/0.

Figure 8. Variation of flow with SP dosage of mix with Slag/Fly ash 75/25.
4.2 Initial and final setting time

The variation of initial and final setting time for different paste mixes with a/b ratio is shown in Figure 11 and Figure 12. The variation of setting times for different mixes with varying SP dosage is represented in Figures 13 to 20. From the study, it was found that both initial and final setting time increases tremendously with increase in the a/b ratio. Also, the use of SNF was found to be less effective in prolonging the setting time of alkali activated geopolymer paste as there was only a marginal rise in setting time of paste with increase in SP dosage. It is notable that the mix with 25% slag and 75% fly ash has not attained final setting even after 24 hours in ambient conditions (at a/b ratio of 1).

![Figure 9. Variation of flow with SP dosage of mix with Slag/ Fly ash 50/50.](image)

![Figure 10. Variation of flow with SP dosage of mix with Slag/ Fly ash 25/25.](image)

![Figure 11. Variation of IST with a/b ratio.](image)

![Figure 12. Variation of FST with a/b ratio.](image)

![Figure 13. Variation of IST with SP dosage for paste with slag / flyash 100/0.](image)

![Figure 14. Variation of IST with SP dosage for paste with slag / flyash 75/25.](image)
5. Conclusions
This study is conducted to examine the effect of dosage of superplasticizers (0 to 3%) on the rheological properties of alkali activated fly ash and slag composites with varying a/b ratios. Investigations to understand the effect of superplasticizers and alkali content on the behaviour of geopolymer paste were carried out using mini slump cone and vicat apparatus.

From the experimental program conducted on the geopolymer paste, it was found that as a/b ratio increases both final and initial setting time of the geopolymer paste was found to be increasing tremendously. The use of SNF is not found to be much effective in prolonging the setting time of alkali activated geopolymer paste. As SP dosage increases, increase in the setting time is marginal.

8
only and hence a superplasticizer compatible for the geopolymer composition need to be developed. It was observed that mix with a/b ratio 1.0 with 25% slag and 75% fly ash has not attained final setting even after 24 hours. Few geopolymer mixes had initial setting time more than 150 min and final setting time less than 350 min.

The mini slump cone test conducted on the paste shows that as a/b ratio increases, flow measured was increasing and the increase was found to be nominal at higher a/b ratios (> 0.7) and then it becomes constant. The a/b ratio above which the flow becomes a constant can be defined as saturation a/b ratio. There was a minimal increase in flow of the geopolymer paste with SNF dosage. Also, it was observed that as a/b ratio increases, stiffening of alkali activated paste get prolonged.

6. References

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