Effect of superplastizicer type on the fresh and strength properties of alkali activated slag composites

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Abstract. Nowadays, the demand for green concrete has increased due to the greenhouse gas emissions and uncontrolled pollution from the cement industry. At the same time, the green concrete should exhibit better mechanical properties and durability characteristics when replacing conventional concrete without compromising on the fresh properties. A better solution for the production of green concrete is to use air cured Alkali Activated Slag (AAS) composites, an innovative and sustainable binding material with very low carbon footprint. However, AAS exhibits demerits such as quick setting and poor workability and this demands the use of superplasticizers in such binder systems which are less explored thus far. Hence, this paper presents a study on the influence of superplasticizer type on the fresh and strength properties of AAS mortar. Paste/mortars were prepared with alkali activators composed of sodium silicate and sodium hydroxide and tested to study the setting times, workability, and evolution of compressive strength. It is found that the fresh properties are improved by increasing the alkali to binder ratio and the dosage of superplasticizer. Both sulphonated naphthalene formaldehyde (SNF) and polycarboxylate ether (PCE) based admixtures were found to be effective in alleviating the negatives of air cured alkali activated paste/mortar systems.

1. Introduction
Alkali-activated binders (AAB) are considered as a promising sustainable future construction materials, 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 which is more sustainable. Concrete made from alkali activated binders (called geopolymer concrete (GPC) or alkali activated concrete (AAC)) can be tailor made to possess superior properties with respect to strength and durability. The development of mechanical strength of GPC is 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 use of modern
generation chemical admixtures which were successful in conventional cement concrete systems could be a best option to solve this issue in geopolymer systems without the loss of strength.

The commonly researched superplasticizers in Alkali Activated Materials (AAM) are Lignosulphonates (WRRs), Sulphonated melamine formaldehyde (SMF), Sulphonated naphthalene formaldehyde (SNF) and Polycarboxylic ether (PCE). Bakharev et al. studied the effects of superplasticizer (SP) on the workability and strength characteristics of AAS based GPC and found that the addition of sulphonated naphthalene formaldehyde (SNF) admixtures increases the workability and shrinkage but causes a reduction in compressive strength [1]. Nematollahi and Sanjayan studied the effect of different superplasticizers and activator combinations on workability and strength of fly ash based geopolymer [2]. The authors stated that the effect of superplasticizers on the fly ash based geopolymer directly depends on the type of activator and the SP. Naphthalene based SPs was found to be an effective type for the fly ash based geopolymer activated by only NaOH solution whereas Modified Polycarboxylates based SP is the most effective type for the fly ash based geopolymer activated by NaOH and Na$_2$SiO$_3$.

Puertas et al. investigated the effect of latest generation superplasticizers such as vinyl copolymer and polyacrylate copolymer on the workability and strength of slag based geopolymer paste and mortar [3]. The authors concluded that the effectiveness of both the superplasticizers on the workability of the AAS paste is poor. Palacios and Puertas studied the effect of different superplasticizers on the workability and setting time of fresh alkali activated slag paste [4]. The authors concluded that naphthalene based SP was most effective in NaOH activated slag mix for improving the workability, setting time, compressive and flexural strengths. Palacios et al. further studied the effect of chemical admixtures on the rheological behaviour of alkali-activated slag pastes and mortars [5]. They concluded that for polycarboxylate ether (PCE) added mixes, the yield stress increased nearly twice at the initial stage whereas the SNF admixture had little effect on the yield stress of the paste, in which 0.3% of SNF reduces the yield stress up to 80%. Mithanthaya et al. attempted to develop GPC using suitable mix of industrial waste materials like fly ash, GGBFS, glass powder and aggregates [6]. They observed that naphthalene based superplasticizer improved the fresh and hardened behaviour of GPC. Also the results of strength tests on GPC cubes prepared and cured at room temperature indicate the development of compressive strength up to M40 can be achieved. Although not slag mortar, Ghosh and Ghosh evaluated the workability of fly ash based geopolymer mortar and the effect of alkali content, silicon to aluminium ratio of binders, water content and plasticizer dosages were studied [7]. The authors concluded that increasing the alkali content and silica content reduced the workability. Dosages of naphthalene based superplasticizer above 1% dosage by weight of binder gave marked improvements in the workability. Memon reported the production of self-compacting geopolymer concrete using SP [8]. The author found that the addition of superplasticizer up to 7% dosage not only improved the flowability but also increased the compressive strength. The need for higher dosages of SP was eminent from the study. Xie and Kayali studied the workability performance of fresh geopolymer pastes using slump and mini flow tests [9]. The performance of naphthalene based and polycarboxylate based types of superplasticizers on the class C and class F fly ash pastes were studied and analyzed. Based on the workability results, it was concluded that a polycarboxylate-based superplasticizer was more effective for Class C fly ash but less effective for Class F fly ash.

Laskar and Talukdar tried to develop ultra-fine blast furnace slag (UGGBS) based geopolymer as concrete repairing materials [10]. 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 [11]. Also workability and setting time reduced with the increase of GGBFS and decrease of alkaline liquid.
Based on the literature review, it was eminent that, both PCE and SNF type admixtures modified the mix workability, setting time and liquid demand mainly in fly ash or slag dominated AAM. Literatures on the effect of superplasticizers in geopolymer or alkali activated binder systems are more limited and are mostly restricted on the alkali activated systems made using fly ash and slag. Fly ash geopolymer systems suffer a drawback as heat curing is imperative for its strength and microstructure development. However, alkali activated slag systems can be air cured to get the required strength and durability properties but quite often suffers from poor fresh properties. Few literatures have highlighted that the use of SNF was better while few literatures say that the performance of PCE is better in air cured alkali activated slag systems and the results are still inconclusive and needs further research. The literature study revealed that only very few studies have been conducted in the field of admixture-binder interactions in AAS based systems. Hence, the behaviour of various alkali activated slag systems prepared using different chemical (water reducing) admixtures are to be investigated for the commercial propagation of geopolymer concrete technology, as a promising construction material. Hence this study aims in understanding the influence of superplasticizer type on the fresh and strength properties of alkali activated slag mortar.

2. Materials and Methods

2.1 Materials

Ultrafine ground granulated blast-furnace slag obtained from Astrtra Chemicals, Chennai was used as a binder precursor in the preparation of geopolymer mixes. The activator solution used is a mixture of sodium silicate solution and sodium hydroxide solution. Sodium silicate solution of density 1.59 gm/cm³ with SiO₂ to Na₂O ratio by mass of 2.4 and 40% solid content was used. NaOH pellets with 97-98% purity was mixed with water to make a solution of 10M concentration. The superplasticizers investigated in the study were Ceraplast 300 (SNF based admixture) conforming to ASTM C 494 - 98 Type F and IS 9103-1999, and Cerahyperplast XR W40 (PCE based admixture) conforming to ASTM C 494-03, BS 5075 and IS 9103. Crushed stone sand (M Sand) in the standard gradation conforming to IS 650 was used as fine aggregates in the study.

2.2 Mix Proportion and Synthesis

The alkaline activator solution with alkali to solid binder ratio (a/b) of 0.4, 0.5 & 0.6, using two different types of superplasticizers (SNF and PCE) in different dosages 0%, 1%, 2% and 3% by weight of binder) were used in the study. The alkaline activator solution was prepared by mixing sodium silicate (Na₂SiO₃) and sodium hydroxide (10M NaOH) in the ratio 2.5 by weight. Initial study was conducted in paste and later extended to mortar. Mortar was made with binder to aggregate ratio of 1.5 to simulate the mortar fraction in a medium strength concrete. In the case of paste, solid binders were mixed with alkaline solution using a hand blender. Superplasticizers were then added (to the part of alkaline solution) and were further mixed thoroughly for three minutes. After proper mixing, mini slump cone test and setting time test were conducted on the paste. In the case of mortar, slag was dry mixed with sand. Alkaline solution and SP was added and mixed for three minutes in a Hobart mortar mixer. The testing of mortar was limited to alkali to solid binder ratio of 0.5 and 0.6 with superplasticizer dosages at 2% and 3%. Mini slump cone test and setting time test was conducted on paste to study the flow and setting behavior respectively. The workability of the mortar was tested using flow table apparatus immediately after mixing. The compressive strength of mortar was tested using cubes of size 50mm. The mortar was air cured following the demoulding to obtain the compressive strength at specific ages.

2.3 Tests Methods

2.3.1 Tests on paste

a) Mini Slump Cone Test

The workability of fresh geopolymer paste was studied using mini slump cone test apparatus shown in Figure 1. The apparatus was 3D printed using nylon. The apparatus was placed above the centre of a glass plate. The freshly prepared paste was poured into the truncated conical mould having 19 mm top
diameter, 38 mm bottom diameter and a height of 57 mm, 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 as the final diameter of the spread. From the measured value of average final diameter, the % spread was calculated based on Eq. 1.

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

(1)

Figure 1. Mini slump cone test for measuring the flow of paste

b) Setting Time Test
The initial and final setting time of paste was conducted using Vicat apparatus based on IS 4031 Part 5 (2004) [12]. This method was based on the time of penetration of Vicat needle, in the freshly prepared paste. The time taken for the penetration of 5±0.5mm from the bottom of the mould 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 of the paste.

2.3.2 Tests on Mortar
a) Flow table test
The workability of mortar was studied using flow table apparatus shown in Figure 2. The fresh mortar was placed in 3 layers in the flow table mould having 70mm top diameter, 100mm bottom diameter and 50mm height and each layer was tamped 20 times using tamping rod of 16mm diameter. The tamping pressure was maintained just sufficient to ensure the uniform filling of the mortar in the mould. The mould was then lifted up vertically and the diameter of the spread was measured both with and without 25 blows given to the apparatus in 15 seconds.

Figure 2. Flow table apparatus

b) Compressive Strength Test
The mortar cubes of size 50 mm were cast by filling the mould with mortar in 3 layers and each layer was tamped 25 times using a tamping rod of 16mm diameter. The cubes thus obtained were then subjected to ambient air curing (at temperature of 30 ± 2°C) after removing from the mould. Three cubes were tested for the compressive strength at 3, 7 and 28 days.
3. Results and discussion

3.1 Flow and setting time of paste

The spread of alkali activated slag pastes with varying a/b ratios, type and dosage of SP is measured and the results are summarised in Table 1 for easy comparison. The results suggest that as a/b ratio and dosage of SP increases, there is a tremendous increase in the flow of the paste irrespective of the type of SP. This is because, as a/b ratio and dosage of SP increases, more water is available in the system to enhance the workability of the paste. The highest percentage spread was obtained for AAS paste with a/b ratio of 0.6 (280.58%) for 3% dosage of PCE. In the case of 1% SP dosage, the performance of both SNF and PCE admixtures were comparable at all a/b ratios. For 2% and 3% SP content, it appears that PCE admixture has better performance than SNF admixture with regards to the mini slump cone flow as the % spread was marginally higher for PCE compared to SNF. As SP content was increased from 2% to 3%, it was observed that there is a higher increase in the slump flow irrespective of the type of chemical admixture. Also, the mini slump flow for AAS paste with SP was found to be much higher than that without the SP. It is also inferred that the paste made with a/b of 0.4 even with SP at various dosages up to 3% failed to enhance the flow. Based on the paste results, it can be concluded that both SNF and PCE admixtures were found to be effective in increasing the flow of paste as measured using the mini slump cone test.

| Admixture | Dosage of SP (%) | a/b ratio |
|-----------|------------------|-----------|
|           |                  | 0.4       | 0.5       | 0.6       |
| SNF       | 1                | 31.23     | 136.22    | 201.84    |
|           | 2                | 57.48     | 136.22    | 233.33    |
|           | 3                | 96.58     | 201.84    | 267.47    |
| PCE       | 1                | 31.23     | 136.22    | 214.96    |
|           | 2                | 70.6      | 175.59    | 228.08    |
|           | 3                | 123.1     | 201.84    | 280.58    |
| 0% SP     | 0                | 0         | 83.73     | 109.97    |

Table 2 shows the effect of SP type, dosage of SP (1-3%) and a/b ratios on the initial and final setting time of alkali activated slag paste. It can be noted that alkali activated slag paste undergo quick setting as the setting times were found to be very less. The initial setting time (IST) of the paste was found to vary from 31 to 62 minutes whereas the final setting time (FST) varied from 40 to 90 minutes. For the same dosage of SP, both the initial and setting times increased as a/b ratio is increased. As dosage of SP is increased, setting times got prolonged only marginally. Comparing the SP type, it is inferred that the use of SNF was effective in delaying the setting times when compared to the PCE. This effect is more pronounced at higher dosages of SP and higher a/b ratios. Even though the SNF admixture is more effective in delaying the setting times, there is no significant increase in the setting time with increase in the dosage of SP. Hence, it is suggested to conduct more research at higher dosages of SP or on the addition of any suitable retarders to the paste.
Table 2. Initial and Final setting time of alkali activated slag paste

| Dosage of SP (%) | a/b ratio | PCE IST (minutes) | PCE FST (minutes) | SNF IST (minutes) | SNF FST (minutes) |
|-----------------|-----------|-------------------|-------------------|-------------------|-------------------|
|                 | 0.4       | 31                | 41                | 34                | 40                |
| 1               | 0.5       | 34                | 48                | 43                | 54                |
|                 | 0.6       | 40                | 62                | 58                | 78                |
|                 | 0.4       | 32                | 42                | 35                | 46                |
| 2               | 0.5       | 38                | 50                | 43                | 59                |
|                 | 0.6       | 45                | 69                | 59                | 80                |
|                 | 0.4       | 33                | 44                | 35                | 46                |
| 3               | 0.5       | 43                | 58                | 51                | 65                |
|                 | 0.6       | 55                | 70                | 62                | 90                |

3.2 Workability and strength of mortar

Analysing the results from the study conducted on geopolymer paste, the fresh property of the mix with a/b ratio 0.4 and dosage of SP below 2% was found to be inadequate. Thus, study on the mortar was conducted only on the mixes with a/b ratios of 0.5 and 0.6, and SP dosages limited to 2% and 3% only. Similar to mini slump cone test (given in Eq. 1), final spread diameter of mortar was measured and % spread was calculated by comparing with the initial bottom diameter of the mould. The % spread of mortar thus obtained for the mixes with varying a/b ratios, type and dosage of SP are summarised in Table 3. The flow table test was conducted with and without 25 blows to understand the impact of providing blows in the workability of mortar. The flow was found to increase when 25 blows were given in about 15 seconds.
Figure 3. Flow of mortar at varying a/b ratios, type and dosage of SP

Figure 3 shows the mortar flow for various conditions measured after conducting the test with 25 blows. From the test results and visual observations, it was noted that the flow of the mix increases with increase in a/b ratio from 0.5 to 0.6. Satisfactory flow was observed only for the mix with a/b ratio of 0.6 and SP dosage of 3%. The maximum % spread (or flow) of 130.3% was obtained for the mix with a/b ratio of 0.6 and 3% SNF. Lower dosages of SP (2%) failed to improve the mortar flow considerably. It appears that the mortar with PCE admixture exhibited marginally more flow compared to the SNF admixture at a/b ratio of 0.50, but the results were comparable. The % spread of mortar was lesser when compared to the paste at same a/b ratio, dosage and type of SP. This suggests the need to use higher dosages of SP for mortar and concrete when compared to paste.

Table 3. Flow table test results of AAS mortar

| Alkali to binder ratio | Dosage of SP (%) | Percentage spread without blows | Percentage spread with 25 blows |
|-----------------------|------------------|---------------------------------|---------------------------------|
| 0.5                   | 2% SNF           | 1.66                            | 33.33                           |
| 0.5                   | 2% PCE           | 5.00                            | 34.00                           |
| 0.5                   | 3% SNF           | 46.66                           | 53.00                           |
| 0.5                   | 3% PCE           | 48.33                           | 55.30                           |
| 0.6                   | 3% SNF           | 104.66                          | 130.30                          |
| 0.6                   | 3% PCE           | 102.00                          | 123.00                          |

The compressive strength of air cured AAS mortar was tested on 3rd, 7th and 28th day after the casting and the results are tabulated in Table 4. A typical mortar cube before and after testing is shown in Figure 4. The test results show that the compressive strength decreases with an increase in a/b ratio and also with an increase in the dosage of SP. Among the variables studied, the maximum strength of 1:1.5 alkali slag mortar was obtained for a mix with a/b ratio of 0.5, for 2% PCE by weight of slag. Figure 5 shows the evolution of compressive strength of mortars made with various combinations of a/b ratio, type and dosage of SP. It can be seen that addition of SP retards the early age strength (3 day) compared to 7 and 28 day strength which is similar to conventional cement concrete systems. It can also be observed that the use of SNF admixture gives better or comparable strength when compared to PCE at comparable dosages of SP and a/b ratios. Although PCE gave marginally better results based on the fresh properties, the overall performance of SNF was found to be better from strength considerations. It is also inferred that the use of higher a/b ratio of 0.6, at higher dosages of SP led to a considerable reduction in compressive strength although the workability was found to be good. Based on the test results, it may be inferred that more research needs to be done at lower a/b ratios with higher dosages of SP (3% and above) in order to produce AAS mortar with good workability without compromising on the compressive strength.
a) A typical AAS mortar cube

b) Mortar after testing

Figure 4. AAS mortar before and after testing compressive strength

Table 4. Compressive strength of AAS mortar

| Alkali to binder ratio | Dosage and type of SP | Compressive strength (MPa) |
|-----------------------|-----------------------|---------------------------|
|                       |                       | 3rd day       | 7th day      | 28th day     |
| 0.5                   | 2% SNF                | 48.00         | 54.67        | 67.33        |
| 0.5                   | 2% PCE                | 56.67         | 64.00        | 70.67        |
| 0.5                   | 3% SNF                | 41.33         | 52.00        | 69.33        |
| 0.5                   | 3% PCE                | 34.00         | 51.33        | 56.67        |
| 0.6                   | 3% SNF                | 18.00         | 43.33        | 44.00        |
| 0.6                   | 3% PCE                | 20.67         | 33.00        | 33.00        |

Figure 5. Effect of SP type, dosage of SP and a/b ratio on mortar compressive strength
4. Conclusions
The effect of type and dosage of superplasticizers (0-3%) on the fresh and strength properties of alkali activated slag composites with varying alkali to binder ratios was investigated in the study. Preliminary investigations were carried out by conducting mini slump cone test and setting time test with the aim of understanding the effects of SP on the fresh properties of geopolymer paste. The main conclusions from the study of geopolymer paste are as follows:

- The workability and setting time of paste can be improved by increasing the alkali to binder ratio (or alkaline solution content).
- The mixes with alkali to binder ratio of 0.4 are low workable and hence difficult to be used in practical applications.
- PCE performs better than SNF with regards to mini slump cone test for all the mixes.
- It can be concluded that both SNF and PCE admixtures were found to be effective in increasing the flow of paste as measured using the mini slump cone test.
- SNF is more effective in delaying the setting time than PCE admixture.
- Workability of paste increases with increase in the dosage of SP whereas the effect on retarding the setting times was only marginal. Hence, it is suggested to conduct more research at higher dosages of SP or the addition of any suitable retarders to the paste.

The results obtained from the study on paste led to a conclusion that the mix with a/b ratio of 0.4 was low workable and hence not considered for the study on mortar. Hence, the study on AAS based mortar was limited to the mixes with a/b ratio of 0.5 and 0.6 and the dosage of SP used was limited to 2% and 3%. Fresh and strength properties of geopolymer mortar were evaluated. Workability was investigated using flow table and cubes were subjected to compressive strength test. The main conclusions obtained from the study of geopolymer slag mortar are as follows:

- Similar to the paste results, the workability of mortar was found to increase with increase in the content of alkaline solution.
- The mortar with PCE admixture exhibited marginally more flow compared to the SNF admixture although the results were comparable.
- The test results show that the (air cured) mortar compressive strength decreases with an increase in alkali to binder ratio and also with an increase in the dosage of superplasticiser. The effect of alkali to binder ratio on the strength was found to be more pronounced when compared to the dosage of superplasticiser. Among the mixes studied, the maximum strength was observed for the mortar with a/b ratio of 0.5 and PCE dosage of 2% by weight of slag.
- The use of SNF admixture gives better or comparable strength when compared to PCE at comparable dosages of SP and a/b ratios. Although PCE gave marginally better results based on the fresh properties, the overall performance of SNF was found to be better from strength considerations.
- More experiments are to be conducted at lower a/b ratios but with higher dosages of SP (3% and above) in order to produce AAS mortar with good fresh properties in terms of workability and setting, without compromising on the hardened properties.

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