

Effect of different mixture parameters on the setting time of fly ash/rice husk ash-based geopolymer mortar

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Abstract. The present study investigated the effects of different mixture parameters on the setting time of fly ash/rice husk ash – based geopolymer mortars. Mortar mixtures were prepared using fly ash and rice husk ash as the raw material, activated using a blended alkali activator solution consisting of sodium hydroxide (SH) and sodium silicate (SS). The concentration of SH was varied from 10M to 14M, while the SS/SH ratio was varied to 1.0, 1.5 or 2.0. The ratio of alkali activator solution to binder (A/B) was also varied from 0.45 to 0.55. Fresh mortar mixtures were subjected to setting time measurement at curing temperatures of 80 °C. Cubes of 50 mm size were also prepared and subjected to compressive strength testing at different ages. Results showed that increases in both parameters comprising SS/SH ratio and SH concentration resulted in reduction of setting time, while rise in A/B ratio led to increase in setting time of mortars.

1 Introduction

As a construction material, concrete has played an essential role in the development of infrastructure and residential buildings, required in modern history since the Industrial Revolution. The raw material availability, relatively low production cost, the remarkable physical and mechanical properties of the final products etc., are among the advantages of concrete produced using ordinary Portland cement (OPC). These advantages have made OPC concrete the most used manufactured material worldwide. However, research in recent decades has shown that OPC production results in severe environmental impact in connection with the considerable carbon emissions that are released into the atmosphere.

One of the direct solutions needed to mitigate the environmental impact of OPC, is its replacement with eco – friendly binder systems such as geopolymers. Geopolymers are synthesized inorganic materials produced by activating aluminosilicate raw materials using strong alkali solutions. Generally, aluminosilicate materials used in geopolymer production are either natural pozzolans such as volcanic ash, laterite soil, kaolin clay; or industrial by – products such as fly ash (FA), ground granulated blastfurnace slag (GGBS), rice husk ash (RHA), metakaolin, silica fume etc., [1-3]. Exposure of these raw materials to strong alkali solutions, also called *alkali activators*, leads to the formation of Al and Si monomers in the aqueous environment. During the resulting polycondensation process, the Si and Al species form a polymeric structure consisting of Si, Al and O elements plus some alkalis such as Na and K, to provide charge balance. Several studies have shown that

geopolymer binders exhibit physical and mechanical properties similar or superior to those of OPC. Some studies have also reported superior durability performance of geopolymer binders compared to OPC concretes, in terms of acid attack, chloride attack, shrinkage, alkali-silica reaction (ASR), fire attack etc. Besides, fresh concrete properties such as workability, flowability, setting time etc., also play a crucial role in execution of concrete works in construction [4].

Previous studies [2,5,6] showed that the workability property of fresh geopolymer mixtures is significantly affected by several mixture parameters, unlike in OPC systems where water to cement (w/c) plays the primary role. In the investigations, low calcium FA (Class - F) was activated using a blended alkali activator solution of sodium hydroxide (SH) + sodium silicate (SS). Findings showed that the main mixture parameters influencing workability were alkali activator to binder ratio (A/B), sodium silicate to sodium hydroxide ratio (SS/SH), SH concentration, silicate modulus and solids content of SS used. Several studies have shown that geopolymerization of low calcium raw materials such as Class – F, FA and metakaolin is optimally accelerated at elevated temperatures of between 60 to 90 °C. Such elevated temperature curing is necessary since geopolymer concretes made with low – calcium raw materials typically have relatively longer setting time when cured at ambient temperatures [4].

A study by van Chanh et al. [7] showed that the initial setting time of FA – based geopolymer mortars decreased from 490 to 65 minutes, when curing temperature was increased from 40 to 80 °C, while the final setting time of mortars reduced from 670 to 75 minutes. These results were in agreement with those of another study [8] done on

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FA – based geopolymer pastes, in which it was reported that the initial/final setting times of pastes were reduced from 230/270 minutes to 129/165 minutes respectively, when curing temperature was increased from 65 to 80 °C.

Some studies [9-12] have shown that inclusion of high calcium aluminosilicate materials such as GGBS in geopolymer mixtures, accelerates the hardening process, allowing the mixtures to set at ambient temperatures in a similar manner as OPC mixtures. Incorporation of GGBS into geopolymer mixtures leads to the formation of calcium silicate hydrate (C – S – H) phases along with a geopolymeric gel framework, resulting in higher early strengths and shorter setting time [13,14].

A study by Wijaya and Hardjito [8] showed that mixture parameters including SS/SH and SH concentration, can have significant effects on the setting time of FA geopolymer binder. In their study, the SH concentration was varied from 8M to 12M, while SS/SH was kept constant at 1.0 or 2.0, along with A/B of 0.25. Results showed that the setting time of FA geopolymer mixtures decreased with an increase in concentration of SH from 8M to 12M. This effect of SH was attributed to improvement in capacity of alkali activator solution to dissolve FA particles due to increase in concentration of OH⁻. In turn, the setting time of FA geopolymer mixtures reduced, an effect attributed to the resulting higher amount of soluble Si in the mixture, which improves geopolymerization thereby and reducing setting time. It was further reported that pH level and particle size of FA also influence setting time.

In another study, Topark - Ngarm et al. [15] studied the effect of activator – related mixture parameters on the setting time of high calcium (Class – C), FA – based geopolymer binder that was activated using SS + SH solution. The alkali activator solutions were made at SS/SH ratio of 1.0 or 2.0, while the concentration of SH was 10M, 15M or 20M, while the A/B was kept constant at 0.5. The mixtures prepared using the alkali activator solution containing 20M SH at SS/SH of 1.0, gave the shortest setting time of 28 minutes. It was reported that the setting time of geopolymer mixtures increased with an increase in SS/SH ratio from 1.0 to 2.0, regardless of SH concentration. Rattanasak et al. [16] investigated the effect of FA type on setting time of FA – based geopolymer. Findings showed that mixtures made using Class – C FA gave a relatively shorter setting time than those made with Class – F FA. The shorter setting time durations of Class – C FA geopolymer mixtures were attributed to the presence of a considerable amount of calcium in Class – C FA, which resulted in the formation of a C – S – H phase along with geopolymer gel framework. Nath and Sarker [17] investigated the influence of GGBS inclusion on the setting time of ambient cured FA – based geopolymer mixtures. It was reported that the inclusion of 10% GGBS in FA – based geopolymer mixtures reduced setting time from 1440 to 290 minutes. Further inclusion of up to 30% GGBS reduced setting time to 41 minutes. Results also showed that an increase in A/B from 0.35 to 0.45 resulted in a reduction of initial setting time from 300 to 50 minutes, as well as a reduction of final setting time from 560 to 100 minutes.

Effects of different mixture parameters comprising concentration of SH, SS/SH ratio, and A/B ratio on the setting time of FA/RHA based geopolymer mortars, were investigated in the present study.

2 Experiments

2.1 Materials and methods

A Class – F FA was obtained from Lethabo power plant of Eskom SOC Ltd, South Africa and combined with RHA. In order to reduce the unburned carbon content, RHA was exposed to an elevated temperature of 400 °C for 4 hours using a laboratory electric furnace, at a heating rate of 3 °C per minute [18]. After calcination, RHA was sieved to obtain particle sizes of 0 – 75 µm. Table 1 gives the chemical compositions of FA and RHA materials. Silica sand was supplied by Sallies Silica (pty) Ltd. in particle sizes of 0.8 to 1.4 mm and used as fine aggregate to prepare mortar mixtures. Industrial grade SH flakes were obtained from Kiran Global (pty) Ltd. SH flakes were dissolved in distilled water to prepare SH solutions of 10M, 12M and 14M concentrations. A SS solution of 3.3 silicate modulus and 36% solids content was obtained from PQ Corporation and blended with SH solutions, at varied SS/SH ratios to prepare alkali activator solutions.

Geopolymer mortar samples were made by mixing FA and RHA as the aluminosilicate raw materials, with silica sand and alkali activator solution. The optimum proportions of 90% FA and 10% RHA were adopted from a study by Ardiantoro et al. [19]. Silica sand was mixed with raw materials using a laboratory mortar mixer at a constant aggregate to binder ratio of 2.25. Dry materials were mixed for one minute, then the alkali activator solution was added to the mixture and mixing continued for a further two minutes.

Table 1: Chemical compositions of fly ash and rice husk ash

Oxides	Fly ash (%)	RHA (%)
SiO ₂	54.33	89.20
Al ₂ O ₃	32.49	0.37
CaO	4.22	0.73
Fe ₂ O ₃	3.34	0.60
MgO	0.92	1.53
TiO ₂	1.64	0.03
MnO	0.04	0.14
Na ₂ O	1.83	0.10
K ₂ O	0.71	1.71
P ₂ O ₅	0.52	1.08
LOI	0.56	3.88

LOI* loss of ignition

Cube specimens of 50 mm size were prepared for compressive strength testing in accordance with ASTM C 109 [20]. The fresh cubes were sealed using plastic films to prevent evaporation of liquid contents from the mixtures. Samples were cured at 22 or 80 °C in an oven for 24 hours. All specimens were subjected to the

compressive strength test after 7 or 28 days. Setting time measurement was conducted using a modified Vicat apparatus, as prescribed in ASTM C 807 [21]. For this purpose, fresh mixtures were placed in the specific mould then they were covered with glass plates and stored in the 80 °C oven. The glass plates used for sealing the samples were removed only when the specimens were subjected to setting time measurement using the Vicat apparatus. Figure 1 shows the storage setup of oven – curing for setting time testing of the specimens.

In preparation of mortar mixtures for the compressive strength test, 90% FA + 10% RHA was mixed with alkali activator solutions at constant A/B ratios of 0.45, 0.50, or 0.55. In order to evaluate effects of the alkali activator properties on setting time of FA/RHA geopolymer mortars, mixtures were prepared at various SS/SH ratios made at different concentrations of SH. The ratio of SS/SH was varied from 1.0 to 2.0, while the SH concentrations used were 10M, 12M or 14M, along with varied A/B ratios of 0.45 to 0.55. Table 2 gives mixtures of mortars used for the different tests.



Figure 1 Oven curing storage of geopolymer mortars used for setting time measurements.

Table 2: Mixtures of fly ash/rice husk ash geopolymer mortars

Mix	FA (g)	RHA (g)	Sand (g)	A/B	SS/SH	SH molarity	SS (g)	SH (g)
1	444	49	1110	0.50	1.0	10	111	111
2	444	49	1110	0.50	1.5	10	133	89
3	444	49	1110	0.50	2.0	10	148	74
4	444	49	1110	0.50	1.0	12	111	111
5	444	49	1110	0.50	1.5	12	133	89
6	444	49	1110	0.50	2.0	12	148	74
7	444	49	1110	0.50	1.0	14	111	111
8	444	49	1110	0.50	1.5	14	133	89
9	444	49	1110	0.50	2.0	14	148	74
10	444	49	1110	0.45	1.0	12	100	100
11	444	49	1110	0.55	1.0	12	122	122
12	444	49	1110	0.45	1.0	14	100	100
13	444	49	1110	0.55	1.0	14	122	122

3 Results and Discussions

3.1 Compressive strength

Figure 2 shows the 7 – day and 28 – day compressive strength results of FA/RHA geopolymer mortars that were prepared at varied A/B ratios and subjected to different curing regimes. In all mixtures, the SS/SH ratio and SH concentration were maintained constant at 2.0 and 12M, respectively. It can be seen that the samples that were cured at 80 °C for 24 hours gave higher strengths than those that were cured at room temperature, regardless of the testing age or A/B ratio. The samples that were made at A/B ratio of 0.45 and cured at 80 °C gave the highest 7 – day and 28 – day compressive strengths of 62.3 MPa and 65 MPa respectively but curing of the same mixtures at room temperature led to corresponding strengths that were 78% and 40% lower. The observed improvement in strength development of geopolymer mortars is attributed

to acceleration of the geopolymerization reaction at the higher curing temperature, especially at early ages. Furthermore, rise in the A/B ratio of mortars exhibited an adverse effect on compressive strength. For ambient – cured samples, an increase in A/B ratio from 0.45 to 0.55 resulted in 38% reduction of 28 – day compressive strength, while the oven – cured samples gave only 15% strength reduction. The negative effect of A/B ratio on compressive strength of geopolymer mortars could be attributed to excessive water content in the mixtures, resulting in the formation of a binder matrix that had a relatively higher porosity. This observation was consistent with findings of the previous study [5].

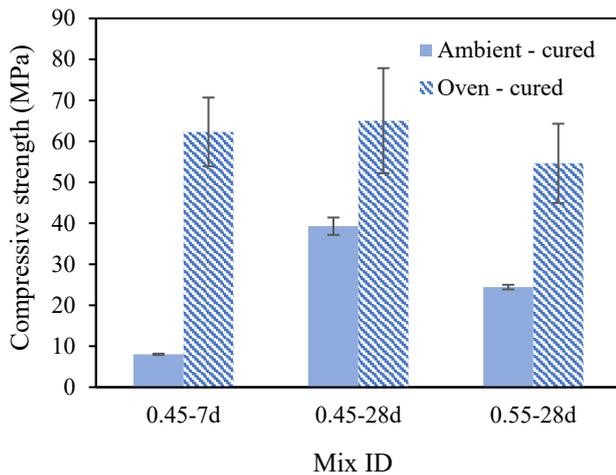


Figure 2 Effect of curing temperature and alkali activator to binder ratio on compressive strength of FA/RHA geopolymer mortars.

3.2 Setting time

Figure 3 shows the effect of SH concentration on the setting time of oven – cured FA/RHA geopolymer mortars, prepared at a constant A/B ratio of 0.5 using alkali activator solutions of varied SS/SH ratios. It can be seen that increases in SS/SH ratio from 1.0 to 2.0 led to significant shortening of setting time, regardless of SH concentration used in the mixtures. The setting time of the mortars that were prepared using 12M SH reduced from 106 to 84 minutes when SS/SH was increased from 1.0 to 2.0. The observed decrease in setting time could be attributed to the presence of additional soluble silica in the mixtures, as provided by SS from the alkali activator, which enhanced the reaction rate at the early stages of geopolymerization. A similar trend in reduction of setting time was observed in mixtures that were prepared using SH concentrations of 10M or 14M.

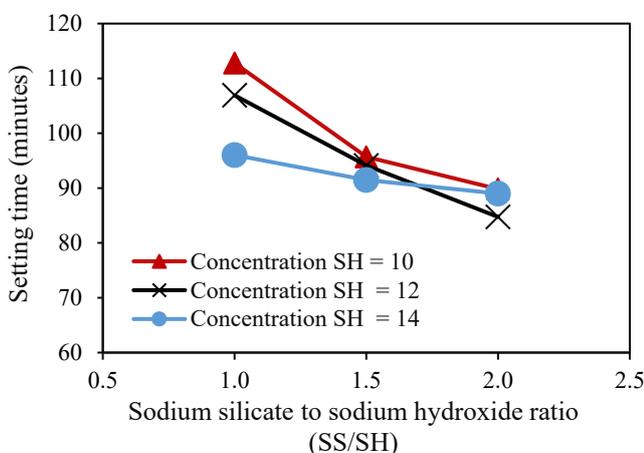


Figure 3 Effect of sodium silicate to sodium hydroxide ratio on setting time of FA/RHA geopolymer mortars cured at 80 °C.

There was also reduction in setting time with increase in SH concentration, regardless of SS/SH ratio, as can also be seen in Figure 4. For samples prepared at an SS/SH of

1.0, increase in SH concentration from 10M to 14M led to a significant reduction in setting time from 113 to 96 minutes, however, the extent of setting time reduction became less pronounced at higher SS/SH ratios. The observed decrease in setting time due to an increase in SH concentration is attributed to the increase in OH^- content in the fresh mixture, which improves the dissolution of aluminosilicate materials. Better dissolution of aluminosilicate materials provides further Si and Al species at the earlier stage of geopolymerization, which accelerates the setting process.

Figure 5 shows the effect of A/B ratio on the setting time of FA/RHA geopolymer mortars that were prepared at an SS/SH ratio of 1.0 using SH at different concentrations, then cured at 80 °C. It can be seen that an increase in A/B from 0.45 to 0.55 did not show a significant effect on setting time of mortars, regardless of the SH concentration. Further Increase in A/B ratio from 0.50 to 0.55, led to an increase in setting time of mixtures made using 12M SH, from 107 to 144 minutes. A similar setting time effect of A/B was observed in mortars made with 14M SH. The observed increase in setting time due to increase in A/B ratio is attributed to the presence of additional water in the mixture, causing a delay in setting time. However, the negative effect of A/B on setting time was more pronounced in the mixtures that were made using 12M compared to those made with 14M SH. This observed difference can be attributed to the higher water content in alkali activators of lower SH concentrations, thereby causing relatively longer setting time durations in the mixtures.

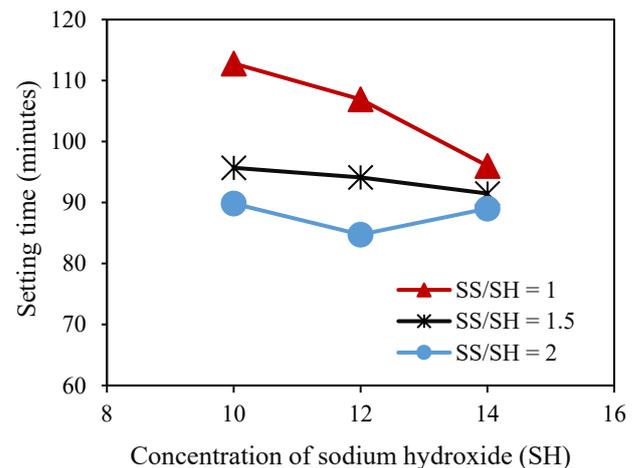


Figure 4 Effect of sodium hydroxide concentration on setting time of FA/RHA geopolymer mortars cured at 80 °C: SS/SH – Sodium silicate to sodium hydroxide ratio.

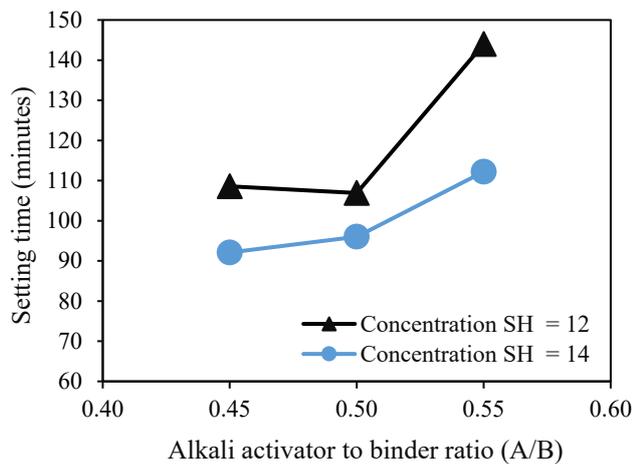


Figure 5 Effect of alkali activator to binder ratio on setting time of FA/RHA geopolymer mortars cured at 80°C: SH – Sodium hydroxide.

4 Conclusions

The effects of mixture parameters on the setting time of fly ash /rice husk ash based geopolymer mortars, were evaluated in the present study. Mortars were prepared of varied parameters consisting of the concentration of sodium hydroxide (SH), sodium silicate to sodium hydroxide (SS/SH) ratio and alkali activator to binder (A/B) ratio. Setting time measurements were conducted on the samples during their curing process at 80 °C. The following conclusions are drawn from the findings:

- Mortars that were cured at 80 °C for 24 hours gave higher compressive strengths compared to those cured at ambient temperature. Geopolymer samples

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that were made using 12M SH at SS/SH of 1.5 and cured at ambient temperature gave 40% lower 28 – day compressive strength than those cured at 80 °C for 24 hours. An increase in A/B ratio from 0.45 to 0.55 led to 38% and 15% reductions for the ambient – cured and oven – cured samples, respectively.

- An increase in SH concentration from 10M to 14M, led to a reduction in setting time of the geopolymer mortars. At a lower SH concentration of 10M, the effect of SS/SH ratio on setting time varied widely as the ratio increased from 1.0 to 2.0. At the higher SH concentration of 14M, effects of various SS/SH ratios converged towards similar setting time results. The observed effect of SH concentration on reduction of setting time is attributed to greater dissolution of raw materials by SH of higher concentrations, which accelerates the reaction rate.
- The setting time of geopolymer mortars decreased with increase in the SS/SH ratio from 1.0 to 2.0. The shortening of setting time with increase in SS/SH, is attributed to the presence of additional soluble silica in the mixtures as provided by SS, which results in higher rates of geopolymerization and shorter setting times.
- Generally, the setting time of mortars was negatively affected upon increase in A/B ratio from 0.45 to 0.55. Mortars that were prepared using 12M SH showed 32% longer setting time due to increase in A/B from 0.45 to 0.55, while mortars made with 14 M SH gave a setting time that was 21% longer. Evidently, the negative effect of A/B on setting time became less pronounced as SH concentration increased

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