EFFECT OF ALKALINE ACTIVATOR, WATER, SUPERPLASTICISER AND SLAG CONTENTS ON THE COMPRESSIVE STRENGTH AND WORKABILITY OF SLAG-FLY ASH BASED GEOPOLYMER MORTAR CURED UNDER AMBIENT TEMPERATURE

***Abstract*—** Geopolymer (cement-free) concrete is the most promising green alternative to ordinary Portland cement concrete and other cementitious materials. While a range of different geopolymer concretes have been produced, a common feature of these concretes is that heat curing treatment which is essential in order to provide sufficient mechanical properties in the early age. However, there are several practical issues with the application of heat curing in large-scale structures. The purpose of this study is to develop cement-free concrete without heat curing treatment. Experimental investigations were carried out in two phases. In the first phase (Phase A), the optimum content of water, polycarboxylate based superplasticizer contents and potassium silicate (Ksil) activator in the mix was determined. In the second stage (Phase B), the effect of ground granulated blast furnace slag (GGBFS) incorporation on the compressive strength of fly ash (FA) and Slag based geopolymer mixtures was evaluated. Setting time and workability were also conducted alongside with compressive tests. The results showed that as the slag content was increased the setting time was reduced while the compressive strength was improved. The obtained compressive strength was in the range of 40-50 MPa for 50% slag replacement mixtures. Furthermore, the results indicated that increment of water and superplasticizer content resulted to retarding of the setting time and slight reduction of the compressive strength. The compressive strength of the examined mixes was considerably increased as potassium silicate content was increased.

***Keywords*—** Fly ash, geopolymer, potassium silicate, room temperature treatment, slag.

I. INTRODUCTION

Geopolymer is a relatively new cement-free material based on industrial by-products such as fly ash, slag, and metakoline. Geopolymer materials can play an important role in the context of sustainability and can provide viable solution for environmental issues related to the production of Portland cement. Cement industry is responsible for the second highest greenhouse gas emissions [1]. Carbon dioxide (CO2) emissions related to cement production are expected to be increased by 100% by 2020, which clearly indicates the likely impacts on global warming indices [2].

Geopolymer binding materials are emerging as a green alternative to Portland cement as they provide comparable mechanical performance and have significantly reduced CO2 emissions [3]. It has been reported that Geopolymer cementitious material present high mechanical strength after curing at 60-75ºC for 24 hrs and remarkable durability properties such as low porosity, fire resistance, freeze-thaw resistance, low thermal conductivity, resistance to aggressive environment [4-6].

Previous research indicates that several factors have an impact on the chemical reactions and subsequently on the strength development of geopolymer concrete including: mixing conditions; water content; chemical activator composition and dosage; raw materials; and curing conditions [7-9]. Xie and Kayali [10] highlighted the importance of water content not only on the workability of fresh geopolymer but also on the hardening phase and on the properties of the hardened concrete. Al-Otaibi [11] investigated the effect of the type and dosage of activator and the improvement of the strength with the increment of the dosage and with the increment of silicate modulus was observed. Nematollahi and Sanjayan [12] investigated the effect of different superplasticizers (naphthalene, melamine and polycarboxylate) on the workability and on the strength of fly ash geopolymer paste activated by two different activator combinations (sodium hydroxide and combination of sodium silicate with sodium hydroxide). Lloyd et al., [13] conducted microstructural analysis on geopolymer concrete activated with silicate-based and sodium hydroxide based solutions, and a more homogeneous microstructure was observed when silicate-based solution was used.

In spite of the advantages of geopolymer materials, the utilization of geopolymer in large production scale is very limited as fly ash based geopolymer shows low reactivity at ambient curing conditions and high temperature curing is essential. There are a few studies focused on the improvement of the mechanical properties of fly ash based geopolymer cured under ambient temperature using additives and admixtures such as silica fume, metakaolin, blast-furnace slag, Portland cement, lime, and nanoparticles [2, 14-16]. Davidovits et al, [17] proposed a user friendly geopolymeric method based on fly ash, slag and using potassium silicate with molar ratio equal to 1.25 as alkaline activator. This user friendly geopolymeric method can improve the strength of fly ash geopolymer concrete as well as reduce costs by avoiding thermal activation and easier handling applications, but the addition of slag can also have drawbacks such as reduced workability and rapid setting times.

The main aim of this study is to investigate the effect of slag to binder ratio, water content, and superplasticizer and alkaline activator contents on the fresh and hardened properties of 50% slag to binder weight ratio of user friendly geopolymer mortars.

II. Experimental Program

A. Materials

Fly ash conformed to BS EN 450 - 1[18] Fineness Category S was used in this study as the main binder. Ground Granulated Blast Furnace Slag (GGBFS) was used as a partial replacement of the fly ash. Silica sand with particle size less than 0.5mm was used as fine aggregates. Chemical compositions as received from the supplier are shown in Table 1. Polycarboxylate based superplasticizer was also used.

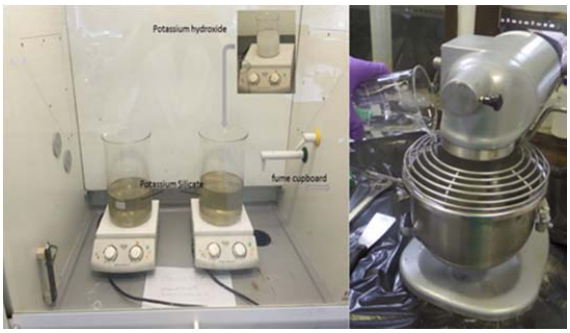
B. Mixing, sample preparation and testing

Potassium hydroxide pearl (85% purity) and commercially available potassium silicate solution (modulus ratio SiO2/Na2O = 2.23, water content= 45-65 wt%, specific gravity 1.6 g/mL) were used as alkali activators. The alkali activator solution was prepared by dilution of potassium hydroxide pellets with distilled water in a fume cupboard (Fig 1a). The solution was left for 24 hours to cool down to room temperature before mixing with potassium silicate solution (mass of KOH solution/Potassium silicate solution = 2.5), to form a solution modulus (Ms=SiO2/K2O) of 1.25.

TABLE I
CHEMICAL COMPOSITIONS OF FA, GGBS AND SILICA SAND (AS RECEIVED FROM THE MANUFACTURER)

Chemical compositions (%)	Fly Ash	GGBS	Silica Sand
Silicon dioxide, SiO_2	59	35	99.73
Aluminum Oxide, Al_2O_3	23	12	0.1
Calcium Oxide, CaO	2.38	40	--
Ferric Oxide, Fe_2O_3	8.8	0.2	0.051
Sulfate trioxide, SO_3	0.27	--	--
Sodium Oxide, Na_2O	0.74	--	<0.05
Potassium Oxide, K_2O	2.81	--	0.01
Magnesium Oxide, MgO	1.39	10	--

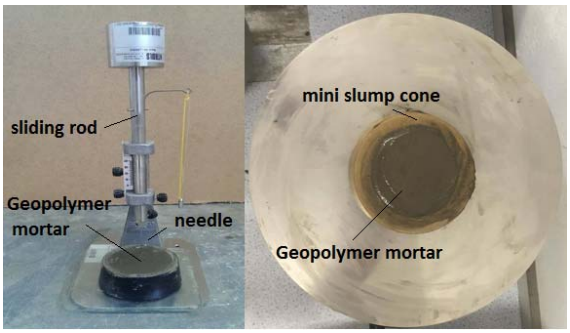
To prepare the geopolymer mortars, specimens were mixed using a 5 L Hobart mixer (Fig 1b). The mixing time and steps followed the procedure proposed in GEOASH [19].



(a) *(b)*

Fig. 1: (a) prepare Potassium silicate solution (b) mixing Geopolymer mortar

Initial and final setting times of the fresh slag/fly ash geopolymer mortar were measured using a Vicat needle as described in BS EN 480-2:2006[20]. Penetration distances were measured every 5 minutes due to rapid setting and hardening of the samples. The initial and final setting times were calculated as the average of two separate measurements of specimens stored under room temperature (21-23ºC). To evaluate the flowability of geopolymer mortar, mini slump tests also known as spread-flow tests were conducted in order to measure the deformability of the examined mixes [21, 22]. During these tests, the cone was lifted straight upwards after filled with the geopolymer and taped in order to allow free flow of the mixture without any jolting (Fig.2b).



(a) *(b)*

Fig. 2: (a) Setting time apparatus, (b) Flowability measurement.

The fresh mixed mortar was then placed in a 50mm cubic mould to determine the compressive strength. The moulds were covered with plastic film to avoid evaporation of water then stored at room temperature for curing (21-23°C) until the day of testing. Compressive strength tests were conducted using compressive machine (Avery Denison 7227) with a capacity of 2000KN and a loading rate of 45KN per min according to ASTM C109 [23].

C. Experimental methodology

A total of 11 mixtures of geopolymer mortar proportions were examined (Table 2). In the first phase of the experimental work, 9 mixtures were used to investigate the effect of varying water content, superplasticizer and alkaline activator to binder ratios on the setting time and on the compressive strength. In the second phase, three mixtures were prepared to study the influence of various slag contents (15%, 25% and 50%) on physical and mechanical properties.

TABLE II
MIXTURES COMPOSITIONS OF FLY ASH/SLAG BASED GEOPOLYMER MORTAR

Chemical compositions (%)	15S	25S	50S
Fly ash	0.85	0.75	0.5
Slag	0.15	0.25	0.5
K2SiO3/binder	0.12	0.12	0.08, 0.01, 0.12, 0.14
Water/binder	0.25	0.25	0.23, 0.25, 0.28
Superplasticizer /binder	0.01	0.01	0.015

III. RESULTS AND DISCUSSION

1) Flowability and setting time tests

The effect of water content and superplasticizer on the setting time of geopolymer mixes was investigated in this study. Setting time tests were conducted based on EN 480-2:2006[20]. Setting time was measured from the end of mixing until the time at which the distance between the needle and the base plate was 4 mm (initial setting time) and 2.5 mm (final setting time). The comparison of the workability (flowability) of the geopolymer mortar in terms of relative slump and setting time for the examined water contents are presented in Fig.3.

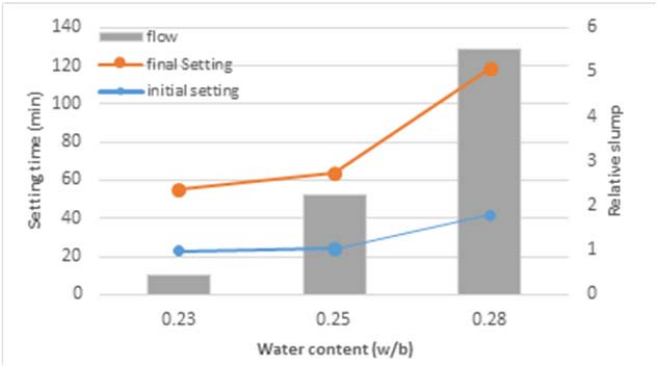


Fig. 3: Effect of water content on Flowability and setting time of geopolymer mortar

Based on the results of Fig. 3, water content considerably affects the setting time of slag and fly ash based geopolymer mortar. The initial and final setting times of 0.23w/b mix were 23min and 32 min respectively, while those of 0.25w/b mix were 24 min and 40 min. By increasing water to binder ratio to 0.28, both initial and final setting times were increased to 40 min and 77 min, respectively.

As shown in Fig.3, increasing water content in the mixture considerably increased the relative slump of the geopolymer mortar. The relative slump was increased by 50% and 100% when the water to binder ratios (w/b) were increased from 0.23 to 0.25 and to 0.28.

The effect of polycarboxylate-based superplasticizer contents on the setting time and flowability of slag and fly ash based geopolymer mortar is presented in Fig. 4.

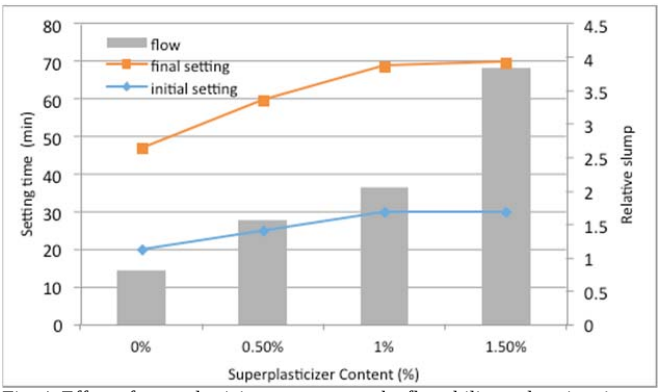


Fig. 4: Effect of superplasticizer contents on the flowability and setting time of geopolymer mortar.

Based on the results of Fig. 4, initial and final setting times were extended as the superplasticizer content was increased. Initial and final setting times without superplasticizer were 20min and 27 min respectively. Initial and final setting times were prolonged to 30 mins and 40 mins respectively when 1% of polycarboxylate superplasticizer was added in the mix. Further increment of the superplasticizer did not significantly affect the results. This is in agreement with a previous study published by Jang et al., [24].

The workability of fly ash and slag based geopolymer mortar without superplasticizer was very low (see fig.4). The flow increased depending on the superplasticizer contents from 0-1.5%. However, the flow sharply increased within 1.5% superplasticizer to binder ratio addition. This can be explained that the improved in the workability is derived from the existence of retarding effect of polycarboxylate-based superplasticizer.

2) Compressive strength results

Three specimens for each mix were tested under compression and the mean compressive strength values are presented in Fig. 5.

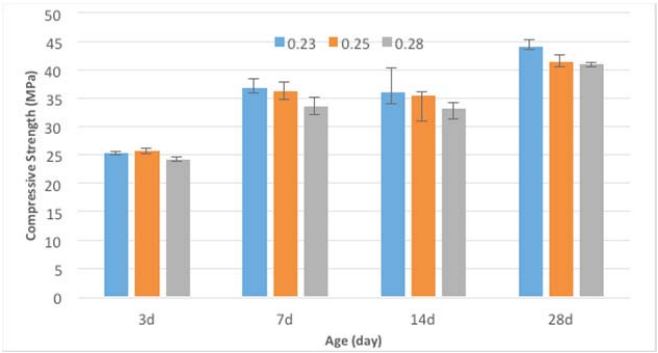


Fig. 5: Effect of water content on the compressive strength of geopolymer mortar.

The results indicate that water content increment did not significantly affect the early strength of geopolymer mortar and a reduction of almost 10% was observed for the 28-days strength. In case of Portland cement concrete, water chemically reacts with the cement to bind concrete components together. In case of geopolymer systems water is only acting as a fluid medium between the dissolved silicates and aluminates ions, providing the required workability [25]. In fact the chemical reaction that occurs in fly ash geopolymers produces water that is eventually expelled from the binder, and water content increment leads to a reduction of the compressive strength of fly ash geopolymer concretes [26].

The effect of superplasticizer content on the compressive strength development of geopolymer concrete mixtures is presented in Fig. 6.

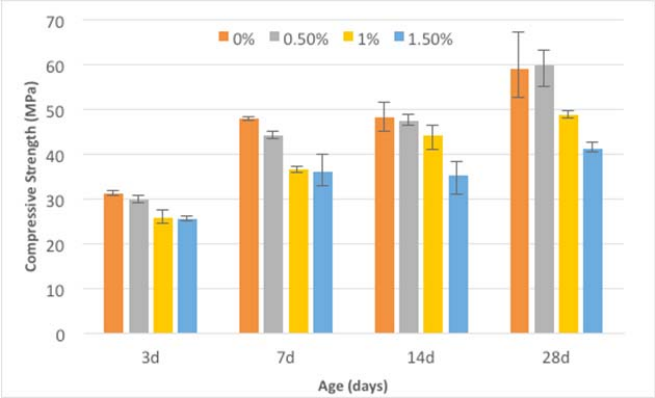


Fig. 6: Effect of superplasticizer content on the compressive strength of geopolymer mortar.

As expected, the mechanical strength is reduced as the superplasticizer content is increased. Based on the results of Fig. 6, the reduction of the compressive strength was found to be in the range of 20-35% and the effect is more important as the age and the compressive strength values are increased. This reduction can be attributed to the dispersion of the binder particles through the adsorption mechanism [25]. Nematollahi et al., [21] examined different types of superplasticizer and based on this study, the addition of polycarboxylate-based superplasticizer resulted to 29% reduction of the compressive strength which is in agreement with the results of Fig. 6.

Alkaline activator content was also found to have an effect on the compressive strength of the geopolymer mortar. Fig.7 shows the relationship between potassium silicate (K_2SiO_3) content and compressive strength in the fly ash/slag geopolymer tested.

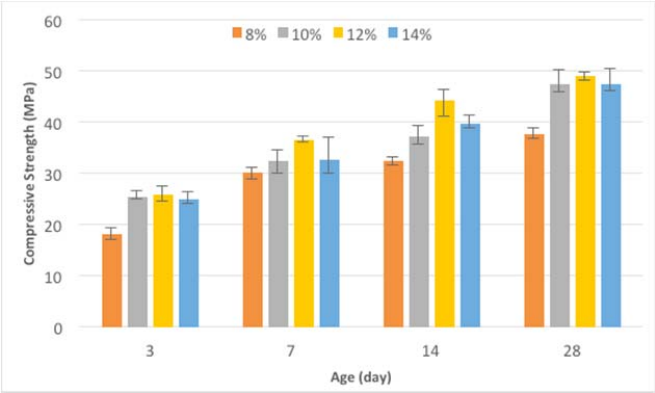


Fig. 7: Effect of alkaline activator on the compressive strength of geopolymer mortar.

Based on the results of Fig. 7, the compressive strength of the examined mixes was increased as the alkaline activators to binder ratios were increased from 8% up to 12%. When higher ratio was used (14%), the compressive strength of the examined mix was reduced. The three day compressive strength of fly ash and slag geopolymer concrete was increased by 40%, and 43%, as the alkaline activator to binder ratio is increased from 8% to 10%, 12% respectively. Regarding the 28days-compressive strength, increment of up to 30% was observed as the alkaline activator to binder ratio was increased. The compressive strength improvement can be attributed to the formation more calcium silicate hydrate gel (C-S-H) composition. On the other hand, excess of alkali solution can increase the amount of water to solid ratio of the mixture leading to higher liquid content which hinders polymerization and subsequent increment of poorly polymerized reaction products [2].

3) Effect of slag content on the fresh and hardened state of geopolymer mortar.

Geopolymer concrete mixtures with 15%, 25% and 50% slag to binder ratio were examined under constant water and alkaline activator content (0.25 and 12% respectively). The influence of geopolymer binder components (slag to binder contents) on the fresh geopolymer mortar is presented in Fig.8.

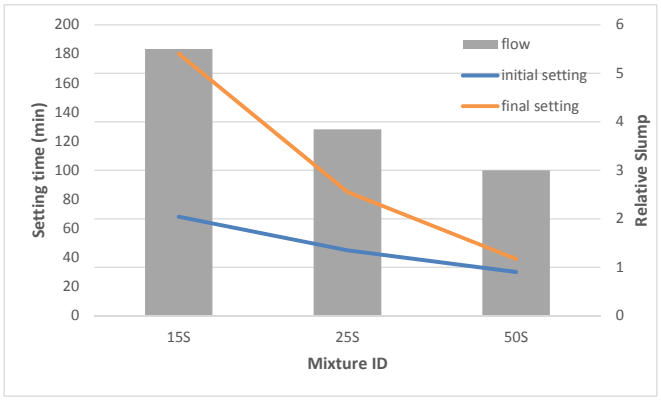


Fig. 8: Effect of Slag on setting time and workability of Geopolymer mortar

The setting time and the workability for geopolymer mortar was significantly reduced by increasing slag content in the mixture. Based on the results of Fig. 8, initial setting time was reduced from 70min to 45min and 30min as the slag content was increased from 15% (15S) to 25% (25S) and 50% (50S). The respective reduction for final setting time was found to be from 180min to 85min and 40min.

The compressive strength results of the mixes with different slag to fly ash ratios are presented in Fig. 9.

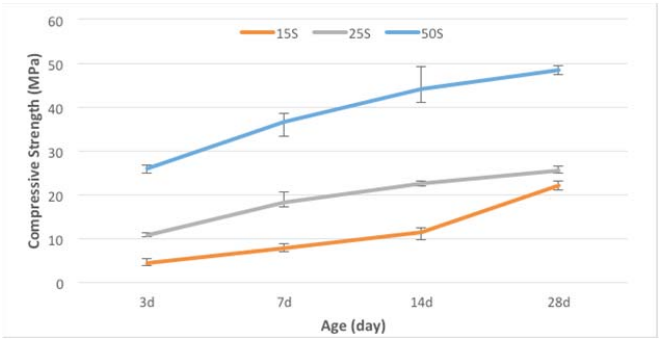


Fig. 9: Effect of slag on the compressive strength of geopolymer concrete

Based on the results of Fig. 9, the strength is considerably increased as the slag content in the mix is increased. At 28 days, the examined geopolymer mixture with 50% wt. ratio of slag to the total binder ratio (50S) achieved 100% higher strength compared to the respective strength of the mix with 15% wt. ratio of slag to the total binder ratio (15S). This is attributed to the fact that incorporation of more slag (source of Ca (Table 1)) in the mix resulted to a matric with higher density due to the formation of additional geopolymerization products of C-S-H and hydrated aluminates calcium. This is in agreement with the findings of a previous study published by Deb et al., [6].

IV. Conclusion

The present study investigated the fresh and hardened properties of slag and fly ash based geopolymer mortar. Fourteen geopolymer mixes were examined with different water, alkaline activator, superplasticizer, and slag contents. Setting time and workability tests were conducted to evaluate the characteristics of fresh geopolymer mortars while compressive strength tests were conducted for the mechanical performance of the hardened mortar. The results can be summarized as follows:

- Relative slump and setting time were increased as the initial water and superplasticizer contents were increased, while at the same time the compressive strength was reduced.
- Alkaline activator (potassium silicate) content was found to be a crucial parameter for the compressive strength. High Potassium silicate content (up to 12% of binder weight) was found to improve geopolymerization process leading to a more compact structure and strength development.
- Flowability and setting time were reduced as the slag to binder ratio were increased. The accelerated geopolymerization reaction is attributed to the presence of slag in the mix.
- The slag to binder ratio considerably affected compressive strength. As the slag to binder ratio was increased from 15% to 50%, the 28 days mean compressive strength was increased from 22 MPa to 49 MPa.

Acknowledgment

The authors gratefully acknowledge the financial support from the Iraqi Ministry of Higher Education and Scientific Research. The authors would also like to thank Hanson Heidelberg Cement Group, PQ Corporation and Sika Limited for providing raw materials.

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