Experimental investigation of the effect of silica fume on geopolymer mortar cured under ambient temperature

Mohammed Al-Majidi [1], Andreas Lampropoulos [1], Andrew Cundy [1]
[1] School of Environment and Technology, University of Brighton, Moulsecoomb, Brighton BN2 4GJ, UK
Phone: +44 (0) 746-2671928, e-mail: m.almajidi@brighton.ac.uk

Abstract

Geopolymer mortar is an environment friendly alternative to conventional cementitious concrete made from by-product aluminosilicate materials with alkaline activator. Silica fume is a by-product of the smelting process in the silicon and ferrosilicon industry which can considerably improve the strength development of high performance concrete [1]. Most of the previous work on geopolymer mortar has focused on the properties of single or binary materials hardened under heat curing conditions, which is considered as a limitation for the production and utilisation of geopolymer concrete at a large scale. In addition, there are no published studies on the effect of silica fume on the generation of geopolymer mortar cured under ambient temperature.

This paper investigates the effect of partial replacement of fly ash with densified, undensified and slurry silica fume (SF) on the setting time, workability and compressive strength of geopolymer mortar cured under ambient temperature. The geopolymer mortar was produced by mixing fly ash and slag (with potassium silicate as alkaline activator) with silica fume in varying proportions. Experimental results indicate that the inclusion of silica fume impacts setting time, workability and strength performance, Key-parameters were found to be the average silica fume particle size and the degree of agglomeration of silica fume particles.

Keywords: Slag, fly ash, geopolymer, silica fume, ambient curing temperature

1 Introduction

Concrete is the most widely used construction material in the world, with a current consumption of $1m^3$ per person per year [2]. Ordinary Portland Cement (OPC) has traditionally been used as the primary binder material to produce the concrete. The huge demand for OPC has resulted in high CO_2 emissions, and depletion of natural resources. Currently, sustainable development is becoming a worldwide goal for human activities, and many researchers are working on the development of alternative cementitious materials in order to reduce drastically the carbon dioxide emissions due to cement production.

A new type of material with cementitious characteristics termed geopolymer concrete has been developed in the recent years [3]. Geopolymer concrete is generally produced by mixing industrial aluminosilicate waste materials (such as fly ash) with alkaline activator. Full replacement of OPC by waste materials can lead to an 80% reduction of carbon dioxide emissions related to cement production [4-6].

Fly ash is an industrial waste material with pozzolanic properties obtained from thermal power plants. Low-calcium fly ash (Class F) has been found to be a suitable material for geopolymer production and can be used as a Portland cement replacement because of its wide availability, useful silica (SiO_2) and alumina-based composition, and reduced water demand [7, 8]. Most previous studies on fly ash based geopolymer cured at ambient temperature highlight its low strength development properties due to a slow polymerisation process [9]. The key factors affecting the potential reactivity of fly ash include the vitreous phase content, reactive silica content, and the particle size distribution [10-12]. Therefore, some researchers have attempted to enhance the reactivity of fly ash based geopolymer by increasing the fineness of fly ash particle size, and by adding quantities of calcium containing materials to react with fly ash particles.

Inclusion of ground granulated blast slag (GGBS) as source of calcium together with fly ash has been investigated, with some favorable results [8]. Ultra-fine particles of amorphous silica, or Silica Fume (SF), is available commercially in various forms depending on material handling techniques (i.e. densified, undensified and water-based slurries). Ivorra et al., [13] studied the effect of silica fume particle size distribution on Portland cement mortar. Based on the experimental results of this study [14], the strength of conventional concrete is increased by using SF with fine particles. This can be attributed to the enhanced

filler effect of SF and to higher pozzolanic reactivity due to the increased specific surface area. However, there are very limited data on the use of such binary blended geopolymer concretes and almost no studies to date on ternary blends of geopolymer concrete.

The present study examines the influence of different particle size distribution of commercial silica fume on the development of fly ash and slag based geopolymer mortar cured under ambient temperature. Ternary geopolymer binder composition, including fly ash, slag and silica fume, with potassium silicate as an alkaline activator have been examined. Extensive experimental studies have been conducted to examine the influence of slag content and particle size distribution of SF on the mechanical properties of geopolymer concrete. Fresh and hardened properties of geopolymer mortar were evaluated by setting time, workability, and compressive strength tests.

2 Experimental Program.

2.1 Materials.

Fly ash conforming to BS EN 450-1 [14] fineness category S was used in this study. This was partially replaced by Ground Granulated Blast Slag (GGBS) and Silica Fume (SF). SF with particle size less than 0.5 mm was used as fine aggregate in this study. The chemical properties of fly ash, slag and silica sand are shown in table 1. Various types of SF were utilized in the tests with different particle sizes distribution; densified (DSF), undensified (USF) and slurry (SSF) (figure.1 and table 2).

Potassium hydroxide pearl (85% purity) and commercial potassium silicate solution (modulus ratio SiO_2 to K_2O equal to 2.23, water content= 45-65 wt. %, specific gravity 1.6 g/mL) were used as alkaline activator. The alkali activator solution was prepared by dilution of potassium hydroxide pellets with distilled water in a fume cupboard. The solution was left for 24 hours to cool down to room temperature before mixing with potassium silicate solution (mass of KOH solution to Potassium silicate solution equal to 2.5), to form a solution modulus equal to 1.25.

Figure. 1. Material used; slag, fly ash and Silica fume forms

Chemical compositions (%)	Fly ash	Slag	Silica Sand
Silicon Dioxide, SiO_2	59	35	99.73
Aluminium 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
Sulphur 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	--
Loss on ignition, LOI	6.7	--	0.09

Table 1: Chemical compositions of FA, GGBS and Silica Sand.

	Bulk density (kg/m^3)
Undensified silica (USF)	130-430
Slurry silica (SSF)	1320-1440
Densified silica (DSF)	480-720
Surface area (BET) (m2/kg)	13,000–30,000
Specific gravity	2.22

Table 2: Bulk density of silica fume types (as received from the manufacturer)

2.2 Mix proportions

A total of eight mixtures were examined with various slag to binder weight ratios (20% and 30%) and different types of silica fume (densified, undensified and slurry). The optimum replacement of fly ash by silica fume in term of workability was 10% for dry silica fume (densified silica, undensified silica), and 5% for

slurry silica. Based on the results of an initial experimental investigation, the optimum mix design (in terms of mechanical strength and workability) is presented in table 3. The molar ratio of potassium silicate solution (K_2SiO_3-used as a chemical activator) remained at the same level for all mixtures at 1.25.

Mix No.	Mix ID	Fly Ash/ Binder	Slag / Binder	Silica fume/ Binder	K2SiO3/ Binder	Water/ Binder	Superplasticizer
1	**20S**	80%	20%	0%SF	12%	25%	1%
2	**20S10DSF**	70%	20%	10%DSF	12%	25%	1%
3	**20S10USF**	70%	20%	10%USF	12%	25%	1%
4	**20S5SSF**	75%	20%	5%SSF	12%	25%	1%
5	**30S**	70%	30%	0%SF	12%	25%	1%
6	**20S10DSF**	60%	30%	10%DSF	12%	25%	1%
7	**20S10USF**	60%	30%	10%USF	12%	25%	1%
8	**20S5SSF**	65%	30%	5%SSF	12%	25%	1%

Table 3: Mixture compositions of geopolymer mortar used in the present study.

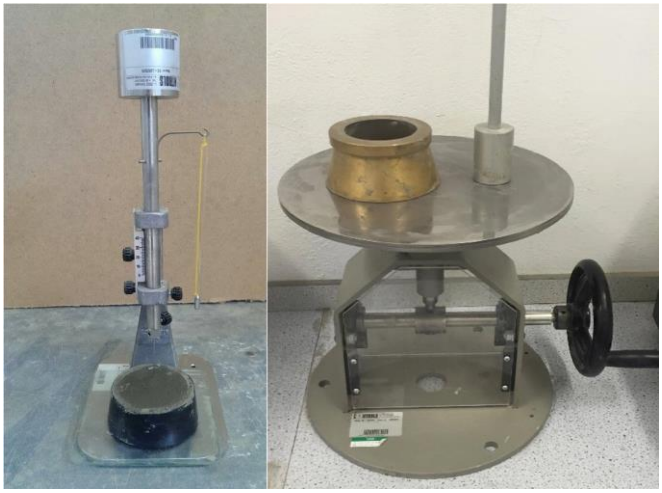
2.3 Mix preparation and testing

All geopolymer mortars were mixed using a 5 liter Hobart mixer. The mixing procedure proposed by GEOASH [15] was used in this study. The liquid phase including the alkali activator potassium silicate solution was prepared in advance and then was mixed with water and superplasticizer 5 minutes prior to the mixing with the solids. The binder powder materials (fly ash, slag and silica fume) were dry mixed for 5 minutes at low speed (140±5r/m) to ensure adequate mixing. The liquid phase was then added to the solid phase and the mixer run at medium speed for 5 minutes. Finally, sand was added and the mixer run for a further 3 minutes to give a total mixing time of 13 minutes. In the case of mixes with slurry silica fume, this was added at the end of the mixing to avoid flash setting, as it very fine and reactive material.

The physical characteristics of silica fume, fly ash and slag powder were determined using particle size analysis (Malvern mastersizer 2000) and scanning electronic microscopy (SEM). For SEM analysis, the examined materials were coated with carbon and imaged using a Zeiss LEO 1455 VP SEM.

For each mortar mixture, two different tests were conducted for fresh state mortar: setting time and workability (figure.2). Initial and final setting times of the

fresh geopolymer mortar were determined using a vicat needle according to BS EN 480-2:2006 [16]. Flow tests were conducted immediately after the end of the mixing in accordance with ASTM C230 [17] and ASTM C1437-07 [18]. A conical brass mould was placed at the center of the table and filled with geopolymer mortar in two layers. Each layer was tamped 20 times with a tamping rod to ensure uniform filling of the mould. When the mould is removed, the mortar changes from a conical shape with a 100mm base to a "pancake" shape. The mortar is vibrated as the flow table rises and drops, through a height of 12.5 mm, 25 times in 15 seconds. The geopolymer flow is the resulting increase in average base diameter of the mortar mass, measured on at least four diameters at approximately equally spaced intervals (figure. 3) [19].



(a) (b)

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

Compressive strength tests were carried out to evaluate the strength characteristics of hardened geopolymer mortar. For each mixture, twelve $50mm^3$ cubes were examined. The specimens were demolded 24 hours after casting and were cured under ambient temperature (21-23°C) until testing. The molds were covered with plastic film to avoid evaporation of water during the curing period. Compressive tests were carried out 3, 7, 14 and 28 days after casting with a loading rate of 45 KN per minute, as specified by ASTM C109 [20].

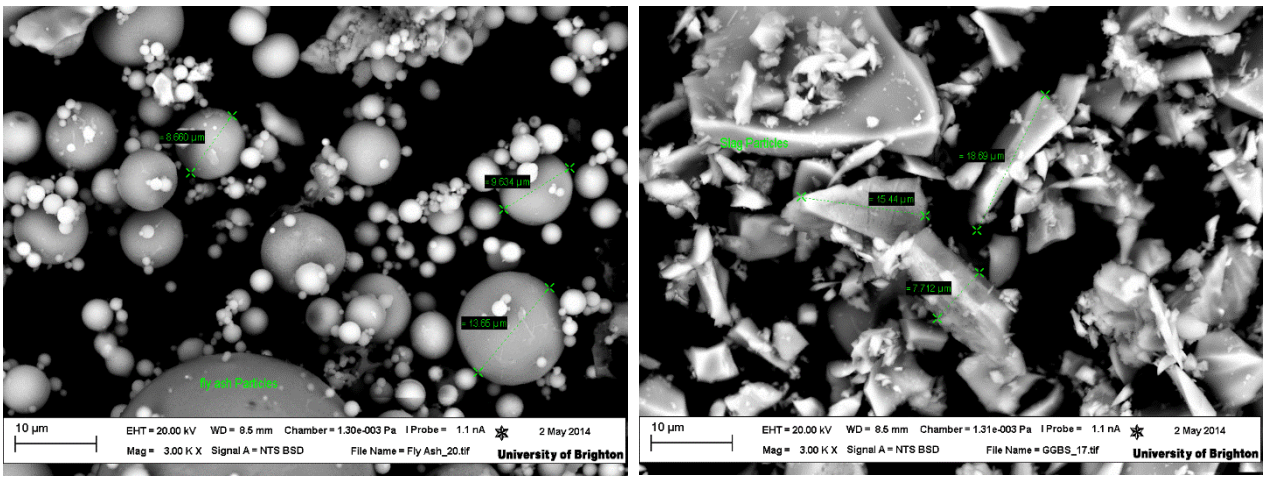
(a) **(b)** **(c)**

Figure.3: flow table test as per ASTM C230 (a) before removal of flow mould, (b) immediately after the removal of the flow mould, and (c) after 25 drops.

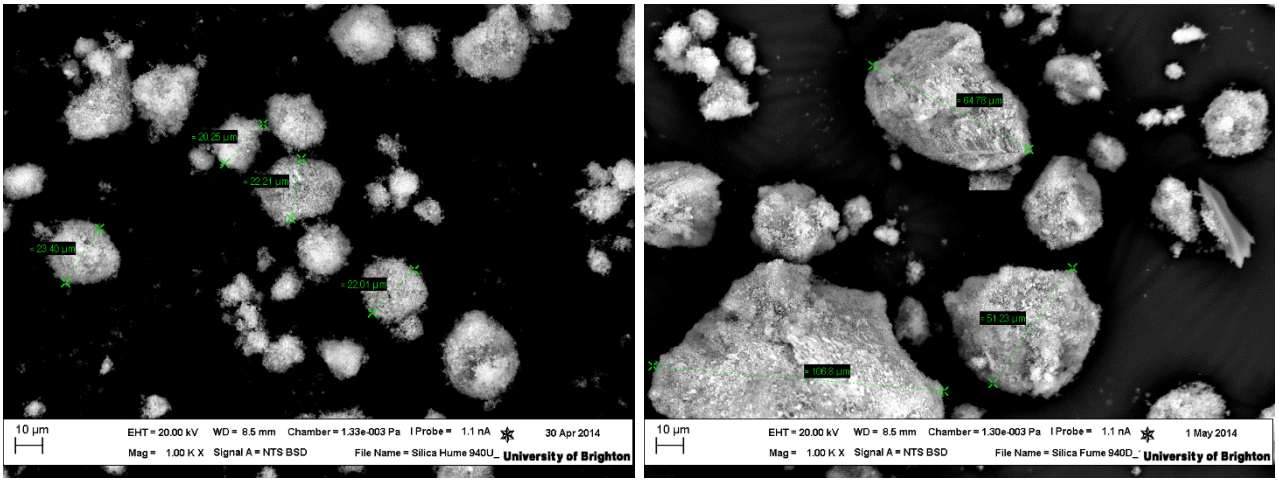
3 Results and discussions

3.1 Particle size analysis

Figure. 4 shows a representative image of the primary particles and agglomerates of slag, fly ash and different silica fume forms. Fly ash and silica fume particles consist of spherical primary particles (figure.4a and 4c); agglomerates of silica fume particles are formed in densified silica fume (figure.4d) while the angular particles of slag are shown in figure.4b.



(a) (b)



(c) **(d)**

Figure.4: SEM images of (a) Fly ash, (b) slag, (c) USF, and (d) DSF

The results of the laser diffraction particle size analysis for slag, fly ash and different forms of silica fume are shown in Figure. 5 and table 4. Table 4 shows the most common statistics used to analyses the particle size: the mean of the particle size (d(0.5)), 10% (d(0.1)) and 90% (d(0.9)) of the total volume of particle size smaller than particular size diameter. It can be confirmed that the aqueous suspension (slurry) with a dry silica fume content of 50% by mass gives the smallest particle size followed by undensified silica fume (USF), and finally densified silica fume (DSF). These results are due to particle agglomeration during the production and packaging procedure of the silica fume. During the formation of silica fume at high temperature (>1000°C), primary particles condense and are bound immediately to clusters of several spheres by sintered junctions through Si–O–Si bonds. Agglomerates of clusters form either when the material cools and is stored in the silo (i.e. undensified silica fume as used in this study) or in the air densification process to produce densified silica fume. It is likely that a finer particle size of silica fume can improve the performance of mortar formulations. It acts physically to optimize particle packing of the concrete or mortar mixture and chemically as a highly reactive pozzolanic with high specific surface area.

	DSF	USF	SSF	Fly ash	Slag
d(0.1)	36.4	4.3	0.1	1.8	1.2
d(0.5)	203.6	37.1	0.3	10.6	4.8
d(0.9)	428.8	126.7	1.5	44.4	22.3

Table 4. Particle size analysis by Mastersizer 2000

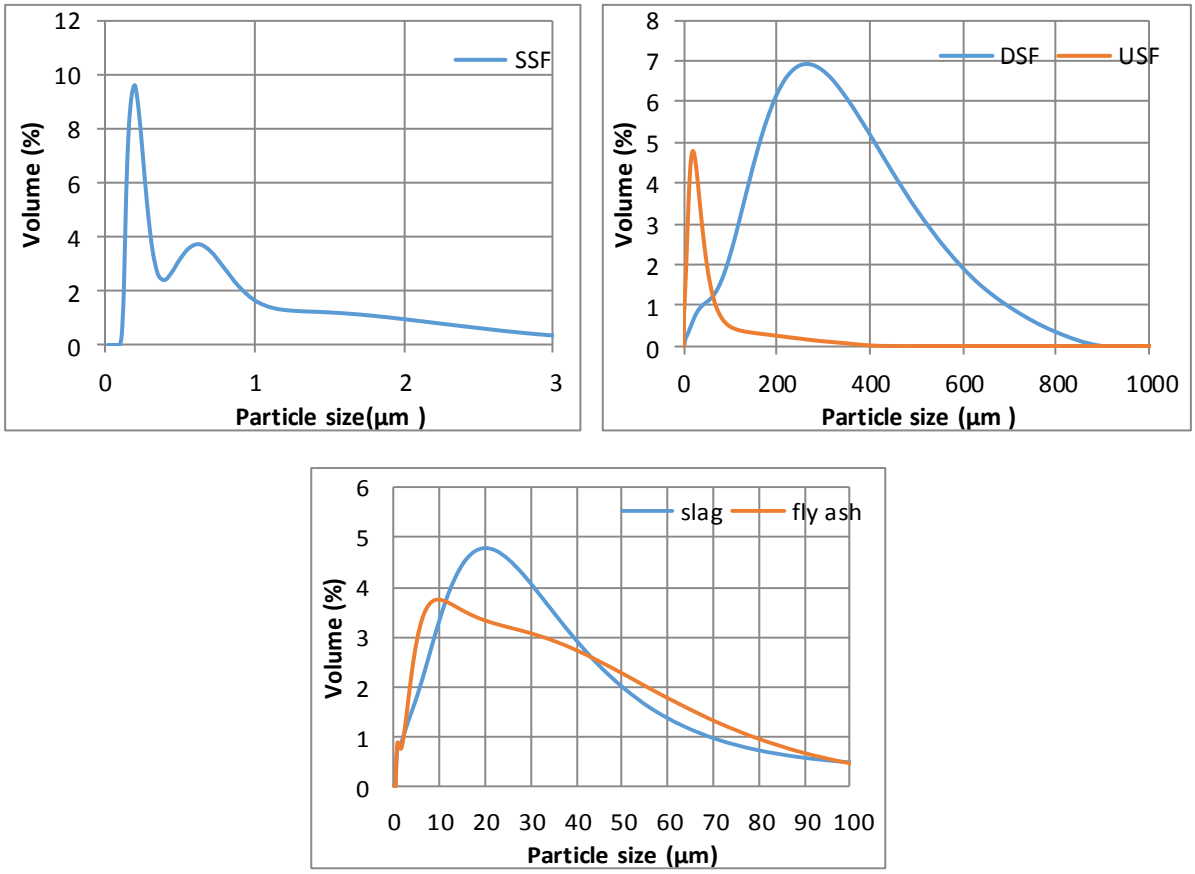


Figure.5: Particle size distribution of (a) SSF, (b) DSF and USF, and (c) Slag and fly ash

3.2 Flow table test.

The workability of the fresh geopolymer mortar determined by flow table testing is presented in table 5.

Mix ID	Flow (mm)
20S	250
20S10DSF	>250
20S10USF	230
20S5SSF	215
30S	210
30S10DSF	210
30S10USF	190
30S5SSF	165

Table 5: The workability properties of geopolymer mortar

The experimental results indicate that the mixture with 20% slag to binder ratio has the highest slump value. As the slag content is increased from 20% to 30%, the slump of the geopolymer mortar is reduced from 250mm to 210mm. This reduction in the workability is attributed to the highly pozzolanic material and subsequently the rapid reaction between the geopolymer binder and the alkaline activator (potassium silicate). The incorporation of densified silica fume in the mixtures results in little change in workability. However, undensified and slurry silica fume incorporation reduces the workability by 16%, 10%, 27%, and 10% compared with the control geopolymer mixtures without silica fume (20S and 30S, respectively). Since very fine silica fume particles have large effective surface area, they rapidly absorb water and thus reduce the workability of the geopolymer mortar.

3.3 Setting time test

Setting time tests were also conducted on the examined mixes and the results are presented in figure. 6.

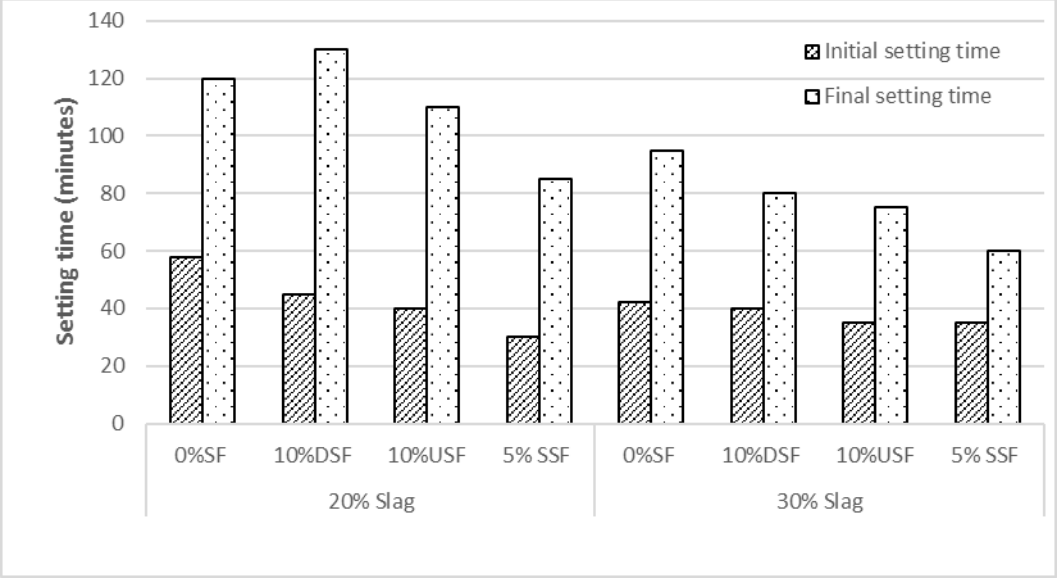


Figure.6: Effect of Silica fume forms and slag content on the initial and final setting time of geopolymer mortar.

Based on the results of figure. 6, it is evident that both initial and final setting time are considerably reduced as the slag content is increased from 20% to 30%. Initial and final setting time of the mix with 30% slag content was further reduced, by 36% and 28% respectively, compared to the respective results of the

mix with 20% slag content. This can be attributed to the increase of CaO content, which is the main chemical component of slag (Table 1), and the subsequent acceleration of the hydration reaction.

The incorporation of silica fume in the mixture also affects both initial and final setting time. In both of the examined mixes with 20% and 30% slag to binder ratios, initial and final setting times were reduced when undensified (USF) and slurry silica fume (SSF) were added to the mix. This reduction is related to the finer particle size and higher surface area of the USF and SSF compared to the larger particle size of densified silica fume (DSF).

3.4 Compressive test

The compressive strengths of all geopolymer mortars at 3, 7 and 28 days are shown in figure. 7.

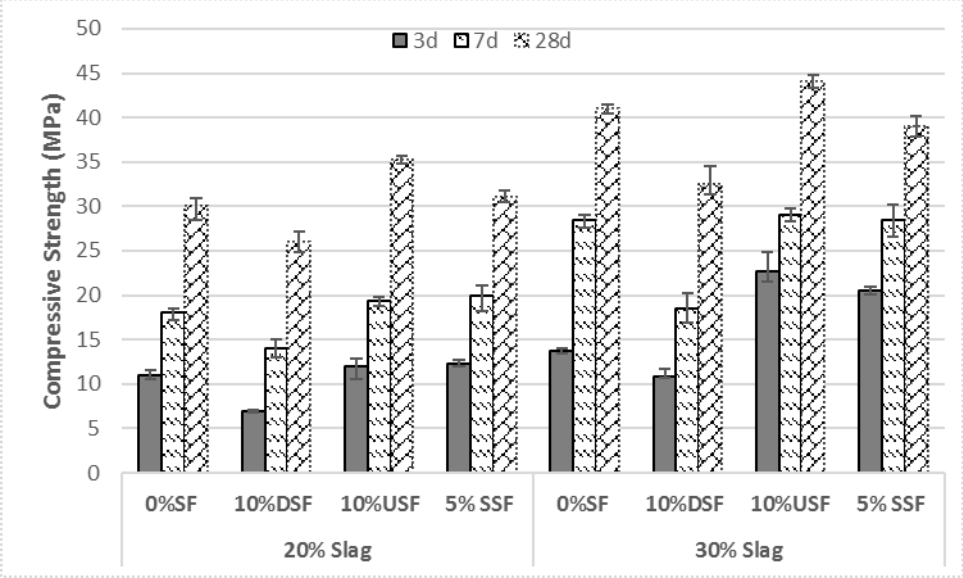


Figure.7: Effect of silica fume on the strength development of geopolymer concrete

It can be clearly seen from the results of fig. 7 that the compressive strength was gradually developed with the age of the specimens. The strength at 3 days was found to be equal to 25%-30% of the 28 days strength. In case of binary blended geopolymer mortar (fly ash and slag), the experimental results indicate that the compressive strength was increased for higher slag content. This is attribut-

ed to the inclusion of high reactive slag particles and to the filling of the pores by formation of more hydration products.

For ternary blended geopolymer mortar mixtures with undensified (USF) and slurry silica fume (SSF), the compressive strength was higher than the strength of geopolymer mortars with binary blended binder. However, the results show that the compressive strength was decreased by inclusion of densified silica fume (DSF).

The particle size distribution of silica fume obviously affects the compressive strength of geopolymer mortar. Undensified silica fume with particle size (37µm) shows higher compressive strength than geopolymer mortars with silica fume particles sizes of SSF (200nm) and DSF (230µm). This development in strength with finer particle size is due to infilling of pores by small particles, acceleration of the geopolymerization process and improvement in interfacial bonding between the binder particles. However, the very fine particles of silica fume (SSF) can agglomerate and show poor dispersion behavior during the mixing, leading to a reduction in strength.

4 Conclusion

An extensive experimental study was conducted to evaluate the effect of silica fume forms alongside various slag contents on the fresh and hardened properties of geopolymer mortar cured under ambient temperature. Workability, setting time and compressive strength were conducted and, from the results of this study, the following conclusions can be drawn;

1- As the slag to binder weight ratio of the examined mixes was increased, flow and setting time were reduced.

2- The inclusion of silica fume in the geopolymer mortar has various effects on the flow of fly ash and slag based geopolymer mortar. In case of undensified and slurry silica in the mix, the workability was considerably reduced. This is attributed to the instantaneous interactions between the very fine silica particles and the alkaline activator, and the formation of a gel characterised by high water retention capacities. The addition of densified silica fume did not significantly affect workability.

3- Compressive strength of geopolymer mortar was increased as the slag content was increased and with the age of the specimens.

4- The addition of fine silica fume had a more pronounced effect on the compressive strength of the geopolymer mortar, particularly in the case of undensified silica fume. The specimens with 10% undensified silica fume had higher compressive strength than the respective control slag/fly ash mortar by 5 MPa and 4MPa for 20S and 30S, respectively. The strength gain of specimens with ultra-fine silica fume (slurry silica fume) was lower than the respective values for specimens with undensified silica fume due to the agglomeration of slurry silica fume particles and their poor dispersion during the mixing.

5- The specimens with 10% densified silica fume showed a reduction of the compressive strength compared to the respective values of the control mixtures.

Acknowledgments

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

Reference

[1] Siddique, R.: 'Utilization of silica fume in concrete: Review of hardened properties', Resources, Conservation and Recycling, 2011, 55, (11), pp. 923-932

[2] Turner, L.K., and Collins, F.G.: 'Carbon dioxide equivalent (CO2-e) emissions: A comparison between geopolymer and OPC cement concrete', Construction and Building Materials, 2013, 43, pp. 125-130

[3] Lee, N.K., Jang, J.G., and Lee, H.K.: 'Shrinkage characteristics of alkali-activated fly ash/slag paste and mortar at early ages', Cement and Concrete Composites, 2014, 53, (0), pp. 239-248

[4] Zhao, F.-Q., Ni, W., Wang, H.-J., and Liu, H.-J.: 'Activated fly ash/slag blended cement', Resources, Conservation and Recycling, 2007, 52, (2), pp. 303-313

[5] Ismail, I., Bernal, S.A., Provis, J.L., San Nicolas, R., Brice, D.G., Kilcullen, A.R., Hamdan, S., and van Deventer, J.S.J.: 'Influence of fly ash on the water and chloride permeability of alkali-activated slag mortars and concretes', Construction and Building Materials, 2013, 48, (0), pp. 1187-1201

[6] Deb, P.S., Nath, P., and Sarker, P.K.: 'The effects of ground granulated blast-furnace slag blending with fly ash and activator content on the workability and strength properties of geopolymer concrete cured at ambient temperature', Materials & Design, 2014, 62, (0), pp. 32-39

[7] Görhan, G., and Kürklü, G.: 'The influence of the NaOH solution on the properties of the fly ash-based geopolymer mortar cured at different temperatures', Composites Part B: Engineering, 2014, 58, (0), pp. 371-377

[8] Nath, P., and Sarker, P.K.: 'Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition', Construction and Building Materials, 2014, 66, (0), pp. 163-171

[9] Adak, D., Sarkar, M., and Mandal, S.: 'Effect of nano-silica on strength and durability of fly ash based geopolymer mortar', Construction and Building Materials, 2014, 70, (0), pp. 453-459

[10] Riahi, S., and Nazari, A.: 'The effects of nanoparticles on early age compressive strength of ash-based geopolymers', Ceramics International, 2012, 38, (6), pp. 4467-4476

[11] Chi, M., and Huang, R.: 'Binding mechanism and properties of alkali-activated fly ash/slag mortars', Construction and Building Materials, 2013, 40, pp. 291-298

[12] Olivia, M., and Nikraz, H.: 'Properties of fly ash geopolymer concrete designed by Taguchi method', Materials & Design, 2012, 36, pp. 191-198

[13] Ivorra, S., Garcés, P., Catalá, G., Andión, L.G., and Zornoza, E.: 'Effect of silica fume particle size on mechanical properties of short carbon fiber reinforced concrete', Materials & Design, 2010, 31, (3), pp. 1553-1558

[14] 450-1:, B.E.: 'Fly ash for concrete. Definition, specifications and conformity criteria', in Editor (Ed.)^(Eds.): 'Book Fly ash for concrete. Definition, specifications and conformity criteria' (31 August 2012., edn.), pp.

[15] D. Antenucci, C.P., G. Lorenzi: 'Understanding and mastering coal fired ashes geopolymerisation process in order to turn potential into profit (GEOASH)', 2009

[16] ‘BS EN 480-2:.Admixtures for concrete, mortar and grout. Test methods.’, in Editor (Ed.)^(Eds.): ‘Book BS EN 480-2:.Admixtures for concrete, mortar and grout. Test methods.’ (2006, edn.), pp.

[17] ‘ASTM C230. Standard specification for flow table for use in tests of hydraulic cement, West Conshohocken (PA): ASTM International; 2002.’, in Editor (Ed.)^(Eds.): ‘Book ASTM C230. Standard specification for flow table for use in tests of hydraulic cement, West Conshohocken (PA): ASTM International; 2002.’ (edn.), pp.

[18] ‘ASTM C 1437–07. Standard test methods for flow of hydraulic cement mortar. West Conshohocken, PA: ASTM International; 2008.’, in Editor (Ed.)^(Eds.): ‘Book ASTM C 1437–07. Standard test methods for flow of hydraulic cement mortar.West Conshohocken, PA: ASTM International; 2008.’ (edn.), pp.

[19] Kondraivendhan, B., and Bhattacharjee, B.: ‘Flow behavior and strength for fly ash blended cement paste and mortar’, International Journal of Sustainable Built Environment, 2015, 4, (2), pp. 270-277

[20] C109, A.: ‘Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 50-mm Cube Specimens).’, in Editor (Ed.)^(Eds.): ‘Book Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 50-mm Cube Specimens).’ (2012, edn.), pp.