EXPERIMENTAL STUDY ON WORKABILITY OF ALKALI ACTIVATED FLY ASH AND SLAG-BASED GEOPOLYMER CONCRETES

K. Arbi[1,*], M. Nedeljkovic[1], Y. Zuo[1], S. Grünewald[2] A. Keulen[3] and G. Ye[1]
[1] Materials & Environment, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, Netherlands
[2] CRH, the Netherlands
[3] Van Gansewinkel Minerals, the Netherlands
* Corresponding author: E-mail: *k.arbi@tudelft.nl*

Abstract: This paper presents an investigation on workability and strength of geopolymer concrete made of fly ash (FA), blast furnace slag (BFS) and a multi-compound activator of Na_2SiO_3 and NaOH solutions. The FA/BFS ratios were 100:0, 70:30, 60:40, 50:50, 40:60, 30:70 and 0:100. The workability of geopolymer concretes was performed by using slump test and controlled by using different types of admixtures. Polycarboxilate, melamine, naphthalene-based superplasticizers (SPs) and retarders were used. The results showed that when alkali activating solution to binder ratio is fixed, a good workability was achieved without SPs for FA rich mixtures. However for BFS rich mixtures a combination of SPs and retarder was needed to reach similar workability and setting. The increase of slag content increased the compressive strength but decreased the workability and setting time. In all mixtures, a good workability with slump values between 20-25 cm and high compressive strength (~70MPa at 7d) were achieved when retarder and superplasticizer were added into the mixtures. For slag based geopolymer concretes, the best performances were found by using N-based SPs. The air content measured for all mixtures was between 2.5-3%.

Key Words: *Fly ash, blast furnace slag, geopolymer concrete, workability, admixtures*

1. INTRODUCTION

Among new binders developed as environmentally sustainable construction products to replace OPC, geopolymers based on industrial by-product materials such as fly ash and blast furnace slag are the most promising alternatives for large-scale production [1-6]. Compared to OPC, FA and BFS-based geopolymers have demonstrated better performances such as low energy costs in the manufacturing process, low CO_2 emission, high early age strength and better resistance to aggressive conditions. However some disadvantages have been reported like the low reaction rate of FA-based geopolymers at room temperature [1] or quick setting and high shrinkage with microcracking formation in alkali activated slag [7]. Heat curing has been proposed and widely used to improve early-age strength of FA-based geopolymers. FA/BFS-based geopolumers have shown attractive technical properties allowing to optimize their engineering properties by altering the proportion of FA and BFS. FA based geopolymers modified with BFS were found as suitable binders for low to moderate strength concrete production at ambient curing condition which would widen their application beyond precast areas and will reduce the cost and energy associated with the heat curing process [8]. It has been reported that the incorporation of slag as a secondary precursor in FA-based geopolymers increased compressive strength [1, 8]. It contributed to refinement of pore structure and thus reduced the transportation of chloride ions in the paste [9]. Most of studies conducted on alkali activated blends of FA/BFS were performed in paste and mortars specimens but in a lower scale in concretes; even though existing bibliography on workability of fresh concrete is scarcely studied [8, 10]. In this work, an experimental study of seven FA/BFS-based geopolymer mixture designs was carried out with the aim to understand the effect of different admixtures on workability, setting time and compressive strength.

2. METHODS AND MATERIALS

Solid precursors used for the preparation of concretes are a FA from VLIEGASUNIE BV and a BFS supplied by ORCEM (Netherlands). FA has a specific gravity of 2440 kg/m^3 and 82% of particles with size less than 45µm, compared to 2890 kg/m^3 and 95% of particles with an average size of 45µm for BFS. Gravel is crushed granite with nominal sizes of 4-16 mm and a specific gravity of 2640 kg/m^3. Fine aggregate is natural sand having a specific gravity of 2620 kg/m^3 and particle size of 0-4 mm. All mixtures were activated by a multi-compound activator of sodium hydroxide (NH) and sodium silicate (WG) solutions. The Na_2SiO_3 solution supplied by BRENNTAG (Netherlands) has a specific gravity of 1350 kg/m^3 and a modulus ratio Ms=3.37. The superplasticizers (SPs) supplied by CUGLA BV and TILLMAN BV (Netherlands) used in this work are as follow: one melamine-based (M), 2 naphthalene-based (N1, N2) and 2 modified polycarboxylates (PC1, PC2). Concrete specimens were produced with the following FA/BFS ratios 100:0, 70:30, 60:40, 50:50, 40:60, 30:70 and 0:100 named S0, S30, S40, S50, S60, S70, S10, respectively. The concretes were produced in 150 mm cubic molds with binder content of 400Kg/m^3, water to binder ratio of 0.52 and a binder to aggregates ratio of 1:4.3 by weight. The specimens were demoulded after 24 h and stored in a curing chamber (95%RH, 20ºC) until testing.

The chemical composition of precursors deduced from XRF data is given in Table 1. FA has lower content of SO_3 (0.64%) and loss on ignition (3.37%), higher amount of SiO_2+Al_2O_3+Fe_2O_3 (85.61) making it suitable for geopolymer applications according to ASTM C618. BFS showed good hydraulic activity based on its basicity coefficient K_b=1.023 and good hydration properties according to its hydraulic modulus H_m=1.7.

Tab. 1. Chemical composition of FA and BFS as deduced from XRF data

	SiO_2	**Al_2O_3**	**CaO**	**MgO**	**Fe_2O_3**	**SO_3**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**L.O.I**
BFS	34.40	11.53	39.17	7.81	1.42	0.07	0.23	0.58	-	-	1.15
FA	54.28	23.32	4.23	1.62	8.01	0.64	0.85	1.97	1.23	0.54	3.37

3. RESULTS

3.1. Effect of different admixtures

In FA/BFS-based geopolymer concretes, the workability becomes difficult to control due to differences between FA and BFS (shape, density, reactivity, chemical composition, etc.). As “w/b” ratio was kept constant for all mixtures, the use of different admixtures (SPs, retarders, etc.) will be helpful to optimize their workability. For that purpose mini slump tests were conducted to determine the flowability of geopolymer concretes. The replacement of FA by slag produced a decrease on setting time making necessary the use of admixtures to improve workability and to delay setting of BFS rich mixtures. A retarder (RT1) and a SP were first used. The slump and compressive strength values after 1 and 7 days are shown in Fig. 1 (left). The SP allowed keeping similar workability for all mixtures (slump ~24cm, relative slump Γ_p≈7cm). Γ_p is defined by the equation $\Gamma_p=(d/d_0)^2-1$ where d is the average of two measured diameters of the paste spread and d_0 is bottom diameter of the conical cone, 20 cm in this study. It can be observed that the retarder increases the 1-day strength in slag rich concretes but no significant changes on 7-days compressive strength were observed compared to mixtures without retarder. No apparent effect of retarder on setting time was observed and all mixtures, except S0, set after 10-30 mn. This indicates that slag reactivity is still higher and expected result from RT1 was not achieved for these mixtures.

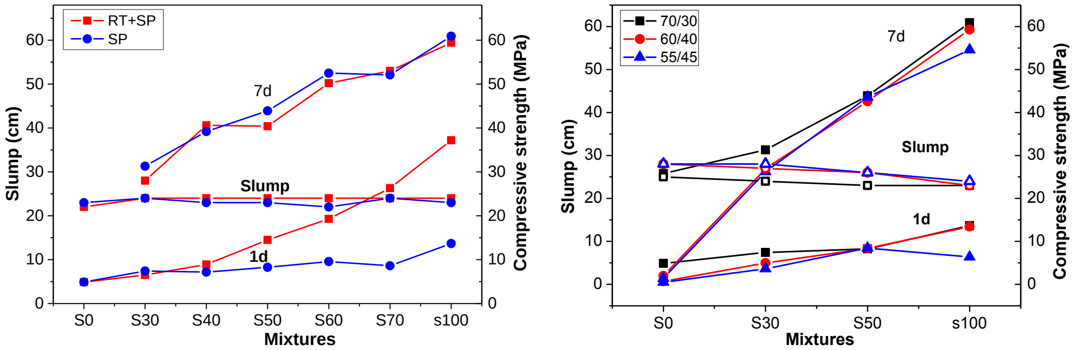

Fig. 1. Effect of different admixtures (left) and activator dosage (right) on workability and compressive strength of FA/BFS concrete

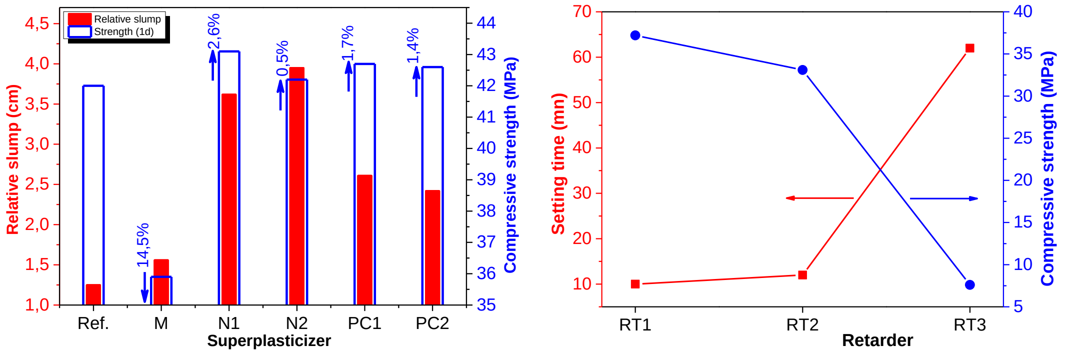

Fig. 2. Effect of admixtures on workability and compressive strength of BFS concrete

3. 2. Effect of activator dosage

In order to decrease the reactivity of slag and consequently increase setting time, we have decreased the amount of silicates from WG by modifying the WG/NH ratio (Fig. 1, right). The results showed that a decrease on Na_2SiO_3 amount decreases both workability and 1-day compressive strength as increasing the slag content. However, setting time was not enhanced (still < 30mn). A drastic decrease on Na_2SiO_3 amount achieved by dilution of the commercial WG has allowed to increase significantly setting time in all mixtures; nevertheless obtained concrete do not develop any strength after 1 or 2 days making this alternative less attractive. Another alternative that could delay setting of slag is to test other retarders. Two admixtures (RT2, RT3) were tested on slag based geopolymer concretes and results are compared with those obtained by RT1 (Fig. 2, right). While the RT2 produced a small decrease on 1-day compressive strength but does not affect the setting time, the RT3 produced an important decrease on 1-day compressive strength and increased setting time from 10 to 65 min.

3. 3. Effect of superplasticizers

The influence of different SPs on workability and strength of BFS-based geopolymer concrete was investigated. Five SPs (M, N1, N2, PC1 and PC2) were used. The relative slump and compressive strength values obtained with and without SP are summarized in Fig. 2 (left). It can be deduced that all SPs improve the workability but in different levels. While with M-based SP only a small increase on relative slump was observed, the N-based SPs improve significantly the concrete workability and relative slump values. The PC-based SPs produce also a clear increase on relative slump. Concerning the effect of SPs on compressive strength, experimental results show that only small increase (1-3%) has been observed when PC or N-based SPs are used. The M-based SP has a negative effect on compressive strength as it produces a decrease of about 14.5% with respect to reference concrete (without SP). From 7d compressive strength (not shown), similar results have been found for M-based SP (decrease of 14.2%). The rest of SPs do not improve geopolymer strength except with the N1-based SP where an increase of 3% was found confirming that N-based SPs (especially N1) are the most suitable for alkali activated slag concrete and could be suitable for FA/BFS-based concrete. The PC-based SPs have been reported as the most suitable for FA-based concrete [11]. They have also showed good results in our mixtures but slightly lower performances compared to the N-based SPs. The air content measured in all mixtures was found between 2.5-3%

4. CONCLUSIONS

From this study it can be concluded that workability and compressive strength can be optimized by tuning the FA/BFS ratio, the activator dosage or by including some admixtures (SPs, retarders, etc.). The inclusion of BFS in the FA concrete increased the compressive strength to 40 MPa at 1 day and near 70MPa after 7 days curing; however this trend is dependent on other factors such as activator (nature, type and dosage), curing conditions, etc. The increase of slag content causes a decrease on both workability and setting time which makes necessary the use of retarder. The best performances were found by using N-based SPs. The use of suitable retarder improves setting time mostly for slag reach mixtures.

Acknowledgements

The authors wish to acknowledge the financial support of the Dutch Technology Foundation (STW) under the project S81.1.13498. ORCEM, VLIEGASUNIE BV, TILLMAN BV AND CUGLA are also acknowledged for supplying BFS, FA and SPs.

REFERENCES

1. Puertas F, Martınez-Ramırez S, Alonso S, Vazquez T (2000) Alkali-activated fly ash/slag cements: strength behaviour and hydration products. Cem. Concr. Res. **30**, 1625-1632.
2. Ismail I, Bernal SA, Provis JL, San Nicolas R, Hamdan S, van Deventer JSJ (2014) Modification of phase evolution in alkali-activated blast furnace slag by the incorporation of fly ash. Cem. Concr. Compos. **45**, 125–135.
3. Kumar S, Kumar R, Mehrotra SP (2010) Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer. J. Mater. Sci. **45**, 607–615.
4. Davidovits J (1991) Geopolymers-Inorganic polymeric new materials. J. Therm. Anal. **37(8)**, 1633-1656.
5. Duxson P, Fernández-Jiménez A, Provis JL, Lukey GC, Palomo A, van Deventer JSJ (2007) Geopolymer technology: The current state of the art. J. Mater. Sci. **42(9)**, 2917-2933.
6. Wang SD, Pu XC, Scrivener KL, Pratt PL (1995) Alkali - activated cement and oncrete. A review of properties and problems. Adv. Cem. Res. **7 (27)** 93-102.
7. Pradip N, Prabir Kumar S (2014) Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition. Constr. Build. Mater. **66**, 163–171
8. Yang T, Yao X, Zhang Z (2014) Quantification of chloride diffusion in fly ash-slag-based geopolymers by X-ray fluorescence (XRF). Constr. Build. Mater. **69**, 109-115.
9. Behzad N, Sanjayan J (2014) Effect of different superplasticizers and activator combinations on workability and strength of fly ash based geopolymer. Mater. Des. **57**, 667–672