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Research Article

Efficacy of Available Superplasticizers on Geopolymers

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Abstract: Geopolymer is a novel engineering binder with lower environmental impacts (CO_2 emission, embodied energy and global warming potential) than Ordinary Portland Cement (OPC). Geopolymers can be synthesized from mixing high alkaline activators by industrial by-products such as fly ash and slag as the aluminosilicate source materials. Superplasticizers (SPs) are one of the common used admixtures added to conventional OPC concrete to improve its workability, rheology and mechanical properties. SPs are intended for use with OPC paste, mortar and concrete. The suppliers of SP do not intend them to be used in geopolymer mixes since SPs are attacked by alkaline solutions and degrade rapidly. However, some SPs can be used with geopolymer with limited effectiveness. This study presents a state of the art review of the effect of different SPs on slag and fly ash based geopolymers.

Keywords: Alkaline activator, fly ash, geopolymer, slag, superplasticizer

INTRODUCTION

Greenhouse gas emissions due to Portland cement manufacture is second only to emissions due to fossil fuel usage. In order to tackle this problem, significant research and efforts are being undertaken to reduce the environmental footprints such as CO_2 emissions, embodied energy and global warming potential in the concrete industry. In this regard, one of the significant breakthroughs in the field of concrete technology in the 20th century was the development of geopolymers. Geopolymer is an alternative cement-less binder to Ordinary Portland Cement (OPC) synthesized from materials of geological origin (e.g., metakaolin) or industrial by-products such as fly ash and slag that are rich in silica and alumina (Diaz-Loya *et al*., 2011). One of the source materials for production of geopolymer is Ground Granulated Blast Furnace Slag (GGBFS) commonly known as slag which is a by-product in the manufacture of pig iron and mainly consists of lime, silica and alumina. About 300 kg of slag will be produced for manufacture of one ton of pig iron (Neville, 1995). Since slag is by-product of iron making industry, the production of slag based geopolymer emits less CO_2 than OPC. The production of OPC emits CO_2 at the rate of 1 ton of CO_2 per ton of OPC. Nearly half of the emissions are due to the energy required to burn the lime at 1800°C and the other 0.5 ton of CO_2 is released due to the chemical release of CO_2 from $CaCO_3$ in making CaO. Previous studies proved that slag based geopolymer concrete has several superior characteristics such as low hydration heat, high early strength and excellent durability in aggressive environment compared with conventional OPC concrete (Roy, 1982; Pu *et al*., 1988; Bakharev *et al*., 1999). In addition to slag, fly ash is also used extensively as the source material for production of geopolymers. Class F (low calcium) fly ash is an industrial by-product of coal-fired power stations (Bakharev, 2005) containing high amounts of silicon and aluminum. The production of fly ash based geopolymer requires approximately 60% less energy than that required for manufacture of OPC resulted in low carbon emission (Li *et al*., 2004). Several studies revealed that heat-cured low-calcium fly ash-based geopolymer concrete possesses high compressive strength, undergoes very little drying shrinkage and moderately low creep and shows excellent resistance to sulfate and acid attack (Hardjito *et al*., 2004, 2005).

It is a common practice to use high range water reducing admixtures commonly known as Superplasticizers (SPs) to improve workability, rheology and mechanical properties of conventional OPC concrete (Palacios *et al*., 2009). SPs are added to OPC concrete to reduce its water content while maintaining a constant workability resulting in higher strength and durability of concrete. Alternatively, SPs can be used to "plasticize" or fluidize the concrete by maintaining a constant water content resulting the concrete to flow better with no change in the compressive strength. There are several types of SPs available, such as Lignosulphonates (Lig), Naphthalene

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(N) and Melamine-based (M) and modified Polycarboxylates (PC). According to Rixom and Mailvaganam (1999), lignosulphonates based SP is considered as the first generation of SPs while melamine-based and naphthalene based SPs are classified as the second generation of SPs where their fluidization mechanism is based on electrostatic inter-particle repulsion. However, modified Polycarboxylate SPs are considered as the third generation (latest generation) of SPs which in addition to electrostatic repulsion benefits from steric repulsion produced by lateral ether chains on the SP's molecule.

The effect and mechanism of SPs in OPC paste, mortar and concrete has been studied in depth by several authors such as Hanehara and Yamada (1999), Brooks *et al*. (2000), Puertas and Vazquez (2001) and Chandra and Björnström (2002) and many others. SPs are not designed to work on geopolymers, however, researchers have attempted to use them in geopolymers to improve the rheology of the geopolymer mixes. SPs have been found to degrade in the alkaline environment provided by the activators and hence found to be not very effective in geopolymers. However, some SPs have found to work to a limited extent in geopolymer mixes probably related to their ability to resist the alkaline activators attack. In this regard, this study presents a state of the art review of the effect of different SPs on workability, strength and rheological parameters (i.e., yield stress and plastic viscosity) of the slag and fly ash based geopolymers.

EFFECT OF SPs ON SLAG BASED GEOPOLYMERS

To date, several studies have been conducted on the effect of the SPs on the slag based geopolymers. Douglas and Barndstetr (1990), for instance, studied the effect of Lig and N based SPs on workability and strength of Na_2SiO_3 activated slag based mortars with two different additives including 2% Lime+1% Na_2SO_4 and 2% Lime+5% fly ash+1% Na_2SO_4. In the case of using Lig based SP with the dosages of 0.2, 0.5 and 1%, respectively of the binder mass, it was concluded that Lig based SP did not improve the workability of the mixes but also reduced the 1-day compressive strength of the specimens with reference to mixes without using SP. In addition, N based SP in the amounts of 0.5, 1, 5 and 9%, respectively by mass of binder (i.e., slag+2% Lime+1% Na_2SO_4) was added and it was observed that this type of SP did not also cause any increase in workability except for mortars with 9% of SP. However, addition of N based SP also decreased the 1-day compressive strength of the mortar specimens with reference to the mixes without using SP. It should be pointed out that these researchers did not investigate the effect of other type of SPs such as M and PC based SPs. They also did not study the effect of using different kind of activators. Moreover, the investigated binder was not pure slag (i.e., additives such as lime, fly ash and Na_2SO_4 were added to the slag).

Bakharev *et al*. (2000) investigated the effect of Lig and N based SPs on the workability and strength of slag based geopolymer concrete activated by three different activators. The investigated activators were mixture of NaOH+Na_2SiO_3 with a SiO_2/Na_2O ratio of 0.75 (for 4% Na by mass of slag) and 1.25 (for 7% Na by mass of slag). A multi-compound activator composed of NaOH (6.3% Na) +Na_2CO_3 (1.7% Na) with a total of 8% Na by mass of slag was also used in their study. Based on the experimental results, they concluded that Lig based SP increased the workability of the slag based concrete activated with all the activators. However, this kind of SP was found to reduce the flexural strength of the concrete and may cause retarding effect in the strength development. On the contrary when N based SP was used, workability of the slag concrete was only increased at the initial stage and then a quick set occurred. With regards to shrinkage, Lig based SP slightly decreased the shrinkage, whereas N based SP considerably increased the shrinkage resulting in reduction in strength of slag based geopolymer concrete. These researchers also did not investigate the effect of M and PC based SPs in their study.

Puertas *et al*. (2003) investigated the effect of latest generation of SPs based upon vinyl copolymer and polyacrylate copolymer on the workability and strength of slag based geopolymer pastes and mortars activated by NaOH+Na_2SiO_3 solution (4% in mass of Na_2O). Their specimens were tested for compression and flexural strengths measurement after 2 and 28 days of casting. They also conducted a calorimetric study on different slag pastes with and without SPs. With regards to strength, they concluded that effect of SP on strength of slag based geopolymer mortars directly depends on the type of SP used. Vinyl copolymer SP reduced the compressive and flexural strengths of the mortars specimens. The reduction in strength was 70-85% and 27-40% for 2 and 28 days strength respectively with reference to the specimens without using the SP. However, polyacrylate copolymers SP had no considerable effect on the strength of slag mortar specimens regardless of the age of the specimens. With regards to workability, it was concluded that both vinyl copolymer and polyacrylate copolymers SPs did not improve the workability of the activated slag pastes. Based on the results of the calorimetric study, vinyl copolymer SP delayed the activation process of activated slag pastes causing lower compressive and flexural strengths of the mortar specimens after 2 days; however, polyacrylate copolymers SP did not change the activation process of the activated slag pastes. This explains that this type of SP does not cause any considerable degradation in the strength of activated slag based mortar. These researchers did not evaluate

the effect of different activators in their study. Following this study, a comprehensive research has been undertaken by Palacios and Puertas (2005).

Palacios and Puertas (2005) studied the effects of five different SPs (2 PC based, one M based, one N based and one vinyl copolymer based SPs) on the workability and setting time of fresh activated slag based pastes. They also investigated the effect of these SPs on compressive and flexural strengths of the activated slag based mortars. Their specimens were cured at 20±2°C and 99% relative humidity and tested after 2, 7 and 28 days, respectively. Two different activators were used in their study including $NaOH+Na_2SiO_3$ with a SiO_2/Na_2O ratio of 3.4 and only NaOH. Two different concentrations of 4 and 5% Na_2O by mass of slag were used for each kind of these activators. All these tests were also conducted on OPC paste and mortars to be compared with the results of the activated slag paste and mortar specimens. Admixtures stability tests were also conducted to investigate the stability of these SPs in high alkaline solutions. These authors concluded that the effect of SPs on alkali-activated slag is considerably different from the effects of these SPs on OPC. This is due to instability of these SPs in high alkaline solutions such as NaOH. According to Palacios and Puertas (2004, 2005), the only type of SP which is chemically stable in NaOH solution as the activator is N based SP causing increase in compressive and flexural strengths of activated slag specimens. N based SP also improved the workability of the paste and delayed the initial and final setting times with reference to slag paste and mortar specimens without using SP. It should be noted that in the case of using OPC the highest reduction in liquid to solid ratio was observed for PC based SPs. With regards to strength, it is found that both the compressive and flexural strengths of OPC mortars were much higher than slag based mortars activated by only NaOH.

Palacios *et al*. (2008) studied the effects of four different SPs (N, M, vinyl copolymer and PC based SPs) on the rheological behavior of activated slag pastes and mortars. Two different activators including $NaOH+Na_2SiO_3$ with a SiO_2/Na_2O ratio of 1.0 and NaOH solution, in both cases with 4% Na_2O by mass of slag, were used. These researchers concluded that the rheology of alkali-activated slag pastes and mortars is considerably depends on the type of the activators used. In the case of using only NaOH solution as the activator, these pastes and mortars follow Bingham model, whereas they match to Hershel-Bulkley model when $NaOH+Na_2SiO_3$ used as the activator. With regards to effect of SPs, it was concluded that none of the SPs used considerably influenced the rhelogical behavior of these pastes activated by $NaOH+Na_2SiO_3$. By contrast, N based SP significantly reduced the yield stress of NaOH activated slag pastes by 80%.

Wang *et al*. (2009) investigated the effect of N and M based SPs on workability, tensile and compressive strength of the slag-metakaolin based geopolymer pastes and mortars activated by $NaOH+Na_2SiO_3$ with 3 different SiO_2/Na_2O ratios of 1.0, 1.2 and 1.4, respectively. The proportion of metakaolin to slag was 3:7. With regards to workability, they concluded that both N and M based SPs increased the fluidity of the paste and the saturation point for N and M based SPs were 2.0 and 2.3%, respectively. With respect to strength, it was concluded that the tensile and compressive strengths of the mortar specimens with the addition of both N and M based SPs were increased initially and then decreased. The optimum content for N and M based SPs were 0.6 and 1.6%, respectively. It should be noted that the investigated binder in this study was not pure slag (i.e., slag-metakaolin by the proportion of 3:7 was used as the binder).

Palacios *et al*. (2009) studied the adsorption of three different SPs (M, N and vinyl copolymer based SPs) on the slag particles in activated slag pastes activated by two different NaOH solution with 0.005 M (pH = 11.7) and 2.57 M (pH = 13.6) concentrations compared with that of the OPC paste. They also investigated the effect of these SPs on the rheological parameters (i.e., yield stress and plastic viscosity) of OPC and slag pastes. It was concluded that adsorption of these SPs on NaOH activated slag pastes is not dependent on the pH of the activator and is 3 to 10 times lower than on OPC pastes. However, the effect of these SPs on rheological properties (yield stress and plastic viscosity) of OPC and slag pastes directly depends on the type of binder in addition to the type and content of the SP. Moreover, in the case of activated slag paste, it also depends on the pH of the alkaline solution. N based SP was the only type of SP that affected the rhelogical parameters of the slag pastes when the activator was 2.57 M NaOH (pH = 13.6) due to its chemical stability in such a high alkaline solution. However, in the case of slag pastes activated by 0.005 M (pH = 11.7), it was observed that vinyl copolymer SP resulted the highest reduction in the yield stress. They also concluded that the amounts of SP needed to achieve similar decrease in the yield stress of the OPC pastes are 10 times higher with reference to 0.005 M NaOH activated slag pastes.

As demonstrated in the review above, the inconsistency in the research results reported is due to diversities in the conditions in which slag based geopolymer pastes, mortars and concrete were prepared such as composition of the slag, type and amount of additives to slag as the binder (such as fly ash and metakaolin), nature and concentration of the activators used, type and dosage of the SPs, time and temperature of curing, etc.

EFFECT OF SPS ON FLY ASH BASED GEOPOLYMERS

On the contrary to several studies on the effects of SPs on slag based geopolymers, few studies have been conducted to investigate the effect of these SPs in the fly ash based systems. Puertas *et al*. (2003), for instance, studied the effect of latest generation of SPs

based upon vinyl copolymer and polyacrylate copolymer on the workability and strength of fly ash based geopolymer pastes and mortars activated by only 8 M NaOH solution. Their specimens were heat cured for 24 h at 85°C and then tested for compression after 2 and 28 days of casting. They concluded that addition of these SPs does not cause any significant changes in strength of the activated fly ash mortars. Moreover, these SPs did not increase the workability of the activated fly ash pastes.

Hardjito *et al*. (2004, 2005) studied the effect of a N based SPs on workability and compressive strength of the fly ash based geopolymer concrete activated by 8 M NaOH solution (28.6%) +Na_2SiO_3 (71.4%) with a SiO_2/Na_2O ratio of 2.0. Their specimens were heat cured for 24 h at 60°C and then tested for compression after 7 days of casting. It was concluded that addition of N based SP improved the workability of fresh concrete. With respect to the compressive strength, they observed that when the dosage of SP is up to approximately 2% by mass of fly ash, the compressive strength was almost unchanged; however, dosages beyond 2% caused degradation in compressive strength (addition of 3.5% by mass of fly ash resulted in 33.3% decrease in compressive strength with reference to the original concrete).

Criado *et al*. (2009) evaluated the effect of Lig, M and PC based SPs on paste rheology (i.e., yield stress and plastic viscosity) of alkali activated fly ash. They concluded that when 12.5 M NaOH solution (85%) +Na_2SiO_3 (15%) with a SiO_2/Na_2O ratio of 3.3 used as the activator the PC based SPs (with a dosage of 0.8%) seems to be the most effective type, however, these researchers have not evaluated the effect of these SP on strength of fly ash paste. Moreover, they have not studied the effect of N based SP in their study. They have not also investigated the effect of the SPs when different activators such as only NaOH are used in fly ash based geopolymer.

Kong and Sanjayan (2010) studied the effect of two different SPs (N based and PC based) in the workability and compressive strength of the fly ash based geopolymer concrete. They concluded that N and PC based SPs did not greatly improve the workability of fly ash based geopolymer concrete activated by 7 M KOH solution (28.6%) +Na_2SiO_3 (71.4%) with a SiO_2/Na_2O ratio of 2.0. Their specimens were cured 24 h at room temperature and then heat cured for 24 h at 80°C and then tested for compression after 3 days of casting. They observed that using these SPs had significant negative effect on the compressive strength of the original concrete. Based on their results, PC based SP with the dosage of 3.3% by mass of fly ash caused significant reduction (54%), while N based SP with the dosage of 1.19% by mass of fly ash caused 21.8% reduction in strength with reference to the original concrete.

Memon *et al*. (2012) studied the effect of a PC based SPs on workability and strength of self compacting geopolymer concrete. Their specimens were heat cured for 48 h at 70°C and then tested for compression after 3 days of casting. They concluded that addition of PC based SP with the dosages of 3% to 7% by mass of fly ash resulted in increase in the workability and the compressive strength of the fly ash based geopolymer concrete activated by 12 M NaOH solution (28.6%) +Na_2SiO_3 (71.4%) with a SiO_2/Na_2O ratio of 2.06 with respect to the concrete containing 3% SPs. However, these researchers did not report the effect of the SP (i.e., increase/decrease in the workability and the strength of the concrete) with respect to the original concrete without any SP.

Recently Nematollahi and Sanjayan (2013) investigated the effects of six different SPs (three modified PC based, two N based and one M based SP) on the workability of fly ash based geopolymer pastes. Based on the experimental results, they concluded that the effect of different SPs on the workability of the fly ash based geopolymer pastes directly depends on the type of the SPs used. In the case of the fly ash based geopolymer pastes activated by 8 M NaOH solution (28.6%) +Na_2SiO_3 (71.4%) with a SiO_2/Na_2O ratio of 2.0, the modified PC based SPs (latest generation) would be the most effective type resulted in 39 to 45% increase in relative slump with reference to the pastes without using any SP.

As illustrated in the review above, the variation in the research results is due to varieties in the conditions in which fly ash based geopolymer mixes were prepared such as composition of the fly ash, nature and concentration of the activators used, type and dosage of the SPs, time and temperature of heat curing, etc. Hence, further research in this area is recommended since the results are not yet conclusive.

SUMMARY AND CONCLUSION

The effect of SPs on workability, strength and rheological parameters (yield stress and plastic viscosity) of slag and fly ash based geopolymer paste, mortar and concrete was comprehensively reviewed in this study. In summary, research results reported in the literature ascertain that SPs do not work the same on geopolymer systems than in OPC systems. The effect of SPs on slag and fly ash based geopolymers directly depends on the type of binder and activators in addition to the type and dosage of the SPs as well as the pH of the alkaline solution. In general, the PC based SPs (latest generation) are the most effective type in the case of fly ash based geopolymer activated by NaOH +Na_2SiO_3 activators. Whereas, in the case of slag based geopolymers activated by NaOH solution, N based SPs (second generation) are the most efficient type. Moreover, in most cases using SPs might decrease the strength of the slag and fly ash based geopolymers with reference to the original geopolymers without using SP.

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