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Polymer blended Geopolymer concrete with supplementary cementitious materials: GGBFS and Fly Ash

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Abstract

For the last few decades, use of industrial wastes such as fly ash and blast furnace slag in various cement concrete structures has gained immense importance. The substitution yielded substantial beneficial action in terms of enhancement of durability, low heat of hydration and better sulphate resisting properties. In order to counteract the diversity of BF slag reactivity from different sources and the poor performance behavior of blended high slag-Portland cement, the proper choice and controlled addition of suitable chemical slag activator has been gaining immense scientific and technological importance that would safely permit maximum percent utilization of granulated blast furnace slag to Portland-slag cement composition. Development of alkali-activated binders with better engineering properties are the new sustainable material for construction along with geopolymers. Geo-polymer materials are inorganic polymers based on alumina and silica units, they are synthesized from a wide range of de-hydroxylated alumina-silicate powders condensed with alkaline silicate in a highly alkaline environment. Using lesser amounts of calcium-based raw materials, lower manufacturing temperature and lower amounts of fuel, result in reduced carbon emissions for geopolymer cement manufacture up to 22%-72% in comparison with Portland cement. Even inclusion of ground granulated slag with class F fly ash can significantly increase the strength and setting of geopolymer binders when cured in ambient temperature. Detailed and extensive research work on geopolymers substituted with slag and fly ash is conducted with addition of various inorganic and organic polymers is presented in this paper.

Keywords: *Blast furnace slag, Class C and Class F fly ash, organic polymers, water soluble polymers, ambient temperature.*

1. Introduction

Geopolymer cement, high alkali (K-Ca-)-Poly (sialate-siloxo) cement, results from an inorganic polycondensation reaction, a so-called geopolymerization yielding three dimensional zeolitic framework. Geopolymer was invented by Davidovits in 1979. Based on industrial by-product such as fly ash and slag, geopolymers can play an important role in construction industry as far as sustainability and environmental isssues are concerned (Duxson , P, *et al,* 2007). It is well observed that 5% of global CO_2 emissions (Lawrence CD, 1998) are originated from the portland cement industries while on the positive side, 80%-90% emissions of greenhouse gases are prevented from by using slag and fly ash (Roy and Idorn, 1992). Geopolymers include three classifications of inorganic polymers which depend on the ratio of Si/Al in their structures:

a) Poly (sialite) (-Si-O-AL-O-)
b) Poly (sialate-siloxo) (-Si-O-Al-O-Si-O-)
c) Poly (sialate-disiloxo) (-Si-O-Al-O-Si-O-Si-O-)

Utilization of geopolymers in cement involves the reaction between an aluminosilicate source such as fly ash, metakaolin or blast furnace slag and an alkaline solution which leads to final hardening of the matrix (Duxson P, et al, 2007), (Davidovits J, 2008), (Davidovits J, 1994). The rate of chemical reaction and chemical kinetics geopolymer concrete is highly influenced by alkaline activators and other curing conditions (Shi C., *et al*, 2006), (Diaz E.I. *et al*, 2010), (Yip C.K. *et al*, 2009). Addition of calcium supplements from calcium hydroxide in geopolymers based on metakaolin highly improved the mechanical properties (Wang K. et al, 2004). Khale and Chaudhury (Islam A, *et al*, 2014) reported that higher compressive strength of geopolymer concrete can be achieved at higher curing temperatures at 85^0C. In comparison with conventional cement materials, geopolymers also have significant advantages such as better mechanical performance (Zhang Z.H., *et al*, 2016), (Zhang Y.J., *et al*, 2012), durability (Mehta A. and Siddique R, 2017) and low thermal conductivity (Duxson , P, *et al,* 2007). F.Pelisser (Pelisser F., *et al,* 2013) in this study presented the effect of metakaolin based geopolymers and found out that hardness and compressive strength of geopolymer concrete after 7 days curing and 0.4GPa and 64 MPa respectively.

2. Addition of various polymers in geopolymer concrete

It is well known that the fragileness and brittleness of geopolymer concrete is a big drawback. Extensive investigations on alkali-activated geopolymers gained widespread importance over the last few years (Palomo A., *et al,* 1999). S.Z. Zhang (Zhang S, 2004) carried out investigation on modifying mechanical performances of kaolinite based geopolymers with water soluble polymers like polyethylene glycol, polyvinvyl alcohol, and polyacrylamide and sodium polyacrylate. Experimental Studies reveal reduced micro cracks and improved cross sectional bending strength is evident due to addition of polymer. P.J. Sun (Sun P.J., and Wu H.C, 2008) clearly concluded that PVA fibers can reduce the brittleness and improve the toughness of concrete.

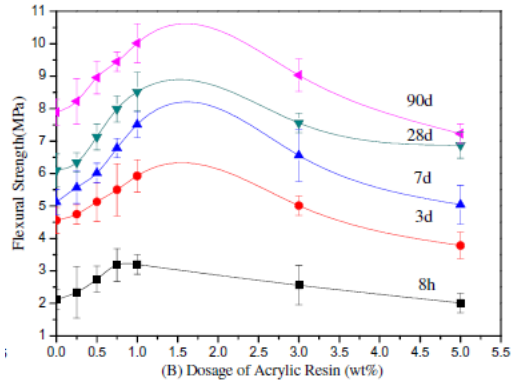

Fig.1 Effect of polyacrylic resin contents on the compressive strength values of GBFS based geopolymer composite at different curing ages (Chen X., *et al*, 2018)

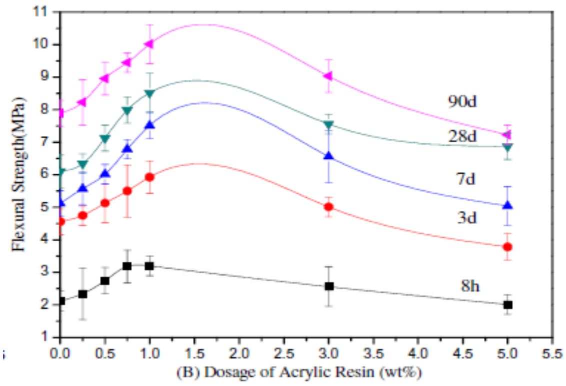

Fig.2 Effect of polyacrylic resin contents on the flexural strength values of GBFS based geopolymer composite at different curing ages (Chen X., *et al*, 2018)

2.1 Strength behavior of slag based geopolymers blended with polyacrylic resins

One such experimental investigation conducted as shown in fig.1 and fig.2, various percentage contents such as 0.25%, 0.5%, 0.75%, 1%, 3% and 5% of polyacrylic resins have been used to check the compressive and flexural strength and even flexural toughness of GBFS based geopolymer concrete . Also, the fig.2 and fig. 3 represents the variation of compressive strength and flexural strength values with respect to various curing ages. Initially the strength values increases followed by progressive and gradual decrease in values.

Specifically, GBFS based geopolymer doped with 1% polyacrylic resin resulted in highest compressive strength of 78.6 MPa at 28 days curing and highest flexural strength of 8.52 MPa at 28 days curing. Polyacylic resin have been found to be highly effective in increasing the strength properties of mortars. Addition of polyacrylic resin also characterizes the behaviour of flexural toughness in geopolymer concrete composites. Incremental content of polyacrylic resin helped in increase slope of the bending modulus curve as shown in fig. 3. With incorporation of 1 % polyacrylic resin content, the flexural toughness reached it' maximum values of 28.4 kN and the flexural toughness index increased by 104.6 %.

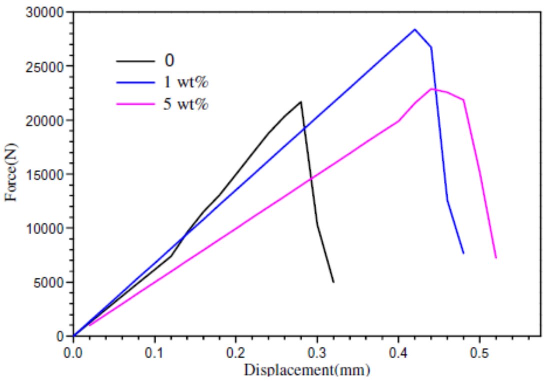

Fig.3 Effect of polyacrylic resin contents on the flexural strength values of GBFS based geopolymer composite at different curing ages (Chen X., *et al*, 2018)

2.2 Behaviour of flexural toughness in slag and fly ash based geopolymers

Further experimental studies on polymer injection of inorganic geopolymers (Zhang S, 2004) reveal that addition of polyacrylic acid (PAA) and sodium polyacrylate (PAA_{Na}) possess the improvement capacity of the compressive strength (max. 29%), cross-bending strength (max. 64.9 %) and volume weight of kaolinite.. Conflicting results such as, polyacrylamide (Pam), polyethylene glycol (PEG) and polyvinyl alcohol (PVA) will greatly decrease the volume weight, weight loss and remnant compressive strength. All these results are shown in fig. 4.

Specifically, in this study, “organic polymers modified kaolinite Na-PSs” also known as OMPs are the subject sample [24]. The relationship of compressive strength of OMPs with respect to polymer loadings is shown in fig. 4.

The improvement in compressive strength follows this trend: PAA> PAA_{Na}>PAm>PEG>PVA. The compressive strength of PAA-OMPS, PAA_{Na}-OMPS, Pam-OMPS and PEG-OMPS all showed increase in strength while PVA-OMPS shows a opposite trend. The main reason behind this can be attributed to high viscosity of PVAs which made the slurry more difficult to mix homogenously and more defects within the sample.

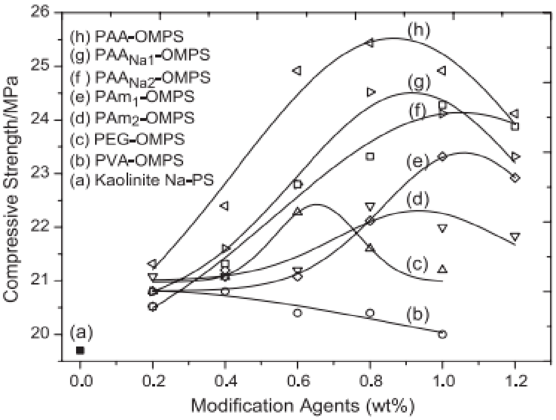

Fig.4 Variation of compressive strength between OMPs with different modifying agents : (a) none, (b) PVA, (c) PEG, (d) Pam$_2$, (e) Pam$_1$, (f) PAA_{Na2}, (g) PAA_{Na1} , (h) PAA (Zhang S, 2004)

3. Geopolymer blended with GGBFS with fly ash with ambient temperature as curing condition

Usually in geopolymer concrete, aggregates are bound by binder which is composed from two parts including aluminasilicates and alkali solution and named geopolymer binder. Proper mix proportioning of concrete results in good workable concrete achieves proper desired strength and durability. In mix design procedure, various parameters such as slump value, w/binder ratio, binder content and aggregate proportions should be considered. In alkali-activated fly ash based geopolymers, ratio of alkali solution to fly ash b/w is usually kept in the range of 0.3 to 0.45 while Table 1 shows a good guideline for selecting target workability and compressive strength (Costa *et al,* 2007).

Few experimental works have been extensively conducted on fly ash blended slag based geopolymer concrete (Deb P.S., *et al,* 2014). In this particular experimental study, class ‘F’ fly ash is used. The chemical composition of fly ash and GGBFS determined by X-ray Fluorescence (XRF results). The molar concentration of the combined alkalies NaOH and Na_2SiO_3 are kept as 14 M. Two different sets of geopolymer concrete mixtures casted: series A and series B. In series A, four geopolymer mixtures were prepared with the activator content of 40% and varying the Sodium silicate/Sodium Hydroxide ratio and the percentage of GGBFS. In series B, six geopolymer concrete mixtures were prepared by reducing the alkaline activator content kept varied from 40% to 35 %. The slag content was 0, 10 or 20% of the binder and the Sodium silicate/Sodium Hydroxide ratio was 2.5 or 1.5 in the mixtures of series B.

Table 1 Guidelines of selecting geopolymer mix design (Bondar D, 2007)

Compressive strength	Workability	Mass ratio of water to polymeric material in solid form
60	Very Low	0.16
50	Low	0.18
40	Normal	0.70
35	Fluid	0.77
30	Fluid	0.74

3.1 Effect of workability in geopolymer cement concrete blended with slag and fly ash

Freshly prepared concrete mixes are prepared and the standard slump value tests are conducted as per ASTM: C 143 -12.

It is observed the smooth spherical texture of fly ash particles combined with lower viscous effect of the alkaline activator solution gives higher flowability to the fresh geopolymer concrete. Alkali activators such as Na_2SiO_3 (SS) and NaOH (SH) solutions, possess more viscous nature, usually makes geopolymer concrete more cohesive and sticky than OPC concrete. Higher slump value indicates less sticky effect and greater workability of geopolymer concrete mixes. Various workability test results indicates decrease in workability with increase in content of slag and decrease in SS/SH ratio. The concrete mix with 20% slag content and 1.5 as SS/SH ratio indicated lowest workability.

Some concrete mixtures with 35% alkaline liquid content showed poor workability as compared to the mixtures previous set when no extra water was added. Therefore, extra water (8 kg/m^3) and superplasticiser (6 kg/m^3) were added to the mixtures of series B in order to improve the workability.

The mixtures were found to have reasonable workability during the casting time. It is quite interesting to observe the workability of a set of concrete mixes decreased with increase of slag content and decrease of the SS / SH ratio.

The slump values with slag content 35%- 40% and SS/SH content resulted values of 215 mm and 245 mm, while for various OPC mixes, the slump values were 105 mm and 150 mm respectively.

Usually the geopolymer concrete mixes indicated more cohesive nature compared to normal OPC mixes. The reason behind this effect can be attributed to difference in the rheology of geopolymer matrix from that of OPC matrix, as described by Khale and Chaudhary (Khale D. and Chaudhary R, 2007). No segregation or bleeding was observed in the mixtures during mixing, compaction and finishing of the concrete. The range of slump values obtained indicates suitable for casting purposes of different concrete members such as beams, columns, slabs and footings. The slump values are well inside the ranges of values reported by other researchers for geopolymer concrete using fly ash only (Olivia M., and Nikraz, H.R, 2012), (Sofi M, 2007), (Sarker P.K, *et al*, 2007).

3.2 Compressive strength parameters of geopolymer cement concrete blended with slag and fly ash

All the variations of compressive strength developed in various geopolymer concrete samples are indicated in fig.5. The graph reveals that the compressive strength initially decreased at the end of 28 days curing but in later stages the strength increased up till 180 days. Trend in variation shows that the compressive strength of the concrete mixes increased with increase in % of slag. The initial strength increase in mixes with 20% slag is 17% higher compared to mixes containing 10% slag. Better results shown when the GGBF slag content is kept 20% with reduced content of Na_2SiO_3/NaOH from 2.5 to 1.5. Incorporation of more calcium based additives resulted in better geopolymer strength results (Van Jaarsveld J.G.S., *et al*, 2002). More compact microstructure of the binder resulted in better strength in various geopolymer mixes.

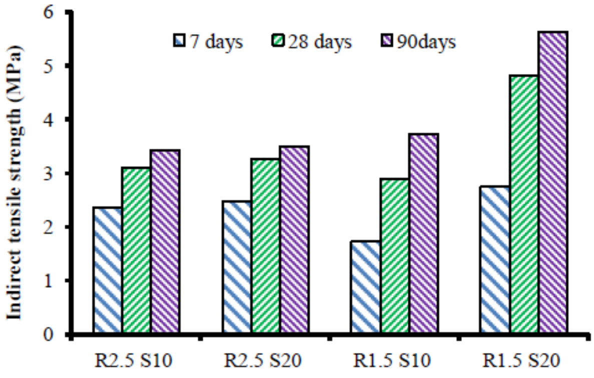

Fig.5 Compressive strength of geopolymer concretes (Deb P.S., *et al,* 2014)

3.3 Tensile strength parameters of geopolymer cement concrete blended with slag and fly ash

Splitting tensile strength tests in accordance with Australian Standard determined the tensile strength values for all the geopolymer and OPC mixes.

The tensile strength values were observed for 7 days, 28 days and 90 days ambient curing conditions. It is obtained from these figures that tensile strength increased with the increase of age for all the mixtures. The tensile strength variation reveals the increase in the respective values with increase in the % content of slag and decrement in Na_2SiO_3/NaOH ratio.

Geopolymer concrete mixture comprising 20% GGBFS and Na_2SiO_3/NaOH ratio of 1.5 gained 55% higher tensile strength than R2.5S10 with 10% GGBFS and Na_2SiO_3/NaOH ratio of 2.5 at the end of 28 days curing.

In another set of samples, geopolymer mixes with only fly ash as binder resulted in lower strength unlike in presence of GGBFS, as a part of the binder. Tensile strength increased from the early age of 7 days with the increase of slag content in the concrete. At 28 days, geopolymer mixes with 10% and 20% GGBFS respectively, achieved 25% and 45% higher strength than R2.5S00. Comparative study on tensile strength value represents the increase in split tensile strength values with decrease in Na_2SiO_3/NaOH content from 2.5 to 1.5.

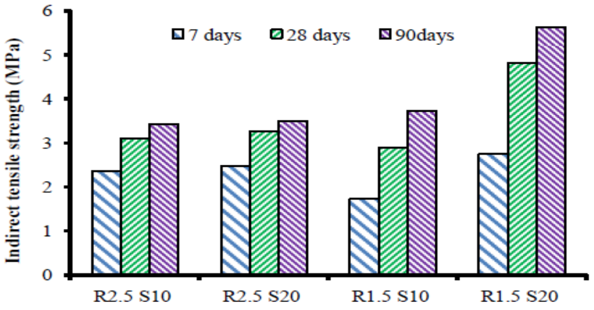

Fig.6 Splitting tensile strength variation of various geopolymer concretes with 40% activators (Deb P.S., *et al,* 2014)

4. Correlation between Tensile strength values with Compressive strength values

Several studies suggest a correlation between tensile strength and compressive strength of conventional OPC concrete. Mainly for alkali activated geopolymer mixes, the ratio of split tensile strength to compressive strength ranges between 0.07 to 0.13. This correlation is similar to that revealed by normal water cured OPC concrete.

Existence of correlation between tensile strength and compressive strength leads to development some simple correlation formulae relating both the strength values. International design codes recommend some correlational formulae. The uniaxial or splitting tensile strengths are usually given in terms of the characteristic compressive strength in these equations with different coefficients and a power of the compressive strength. The Australian standard AS 3600 recommends eqn.1 for OPC concrete at 28 days of age subjected to standard curing.

$$(f_{ct})' = 0.36\sqrt{f_c{}'} \qquad (1)$$

where f_{ct}'= characteristic uniaxial tensile and f_c'= compressive strengths respectively. Due to absence of sufficient data, the mean uniaxial tensile strength (f_{ctm}) is obtained by multiplying the characteristic tensile strength by 1.4. The uniaxial tensile strength is taken as

0.9 times the splitting tensile strength ($f_{ct.sp}$) of concrete. The mean compressive strengths corresponding to characteristic strengths for different grades of concrete are given in the standard.

For 25 to 65 MPa grade concretes, the relationship between the characteristic compressive strength and the mean in-situ compressive strength (f_{cmi}) is given by eqn 2.

The mean in-situ compressive strength (f_{cmi}) shall be taken as 90% of the mean cylinder compressive strength (fcm).

$$f_{cmi} = f_c' + 3.0 \text{ (MPa)} \qquad (2)$$

The ACI 318 code recommends eqn.3 as the approximate relationship between the mean splitting tensile strength and the characteristic compressive strength. The relationships between the mean and characteristic compressive strengths are given by eqn.4, eqn.5 and eqn. 6.

$$f_{ct.sp} = 0.56\sqrt{f_c'} \qquad (3)$$

$$f_{cm} = f_c' + 7.0 \text{ (MPa)} for\ f_c' < 21 \text{ MPa} \qquad (4)$$

$$f_{cm} = f_c' + 8.3 \text{ (MPa)} for\ 21 < f_c \leq 35 \text{ MPa} \quad (5)$$

$$f_{cm} = 1.1f_c' + 5.0 \text{ (MPa)} for\ f_c > 35 \text{ MPa} \qquad (6)$$

Split tensile strength value are calculated from Australian standard (eqn.1 and eqn.2) and the ACI code (eqn.3 to eqn.6) were used to calculate the splitting tensile strengths of the concretes.

Conclusions

From the critical point of view of this review study, few points can surely be recognized.

1) One of the most pivotal parameters such as workability of geopolymer concrete showed decrease in values with the increase of blast furnace slag content together with fly ash in the binder when the other mixture variables remained the same.

2) Investigations reveal that the addition of GGBFS in geopolymers enhanced setting of the concrete at ambient temperature.

3) Workability also decreased with the reduction of the activator to binder ratio from 0.4 to 0.35. Addition of extra water improved workability at the cost of strength.

4) Polymeric activators such as polyacrylamide should be limited to maximum 1 % content in order to derive its maximum effectiveness on compressive strength, flexural strength and even flexural toughness of mortars.

5) Other polymers such as polyacrylic resin can notable increase strength, improve its brittleness and toughness of GBFS based geopolymer, so as to achieve the purpose of toughening modification. Furthermore, FTIR and MAS NMR measurements also conducted to investigate the mechanism of polyacrylic resin modifying the flexural toughness of GBFS based geopolymers, thus to explain the excellent toughening effect.

6) Various mechanical strength parameters at high or elevated temperature found to be dependent on the size of the geopolymer paste specimens.

7.) Conventional superplasticizers such as sulpha based, naptha based, carboxylate based, used with Ordinary Portland Cement, when being applied as an additive to the binder, does not significantly improve the overall workability of the mix. Application of such conventional superplasticizers deteriorates the strength of the geopolymer matrix.

8) Exalted temperature performance in concrete with superplasticizer is also poor.

9) The use of superplasticizers is not beneficial in geopolymer concrete for exalted temperature performance.

10) The difference in thermal coefficient between the geopolymer matrix and its aggregate components is the most likely cause of strength loss in geopolymer concrete specimens at elevated temperatures. Several studies prove this notion.

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