INVESTIGATION OF EARLY COMPRESSIVE STRENGTH OF FLY ASH-BASED GEOPOLYMER CONCRETE

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INVESTIGATION OF EARLY COMPRESSIVE STRENGTH OF FLY ASH- BASED GEOPOLYMER CONCRETE

Lateef N. Assi, Edward (Eddie) Deaver, Mohamed K. ElBatanouny, Paul Ziehl

Abstract

Development of sustainable construction materials has been the focus of research efforts worldwide in recent years. Concrete is a major construction material; hence, finding alternatives to ordinary Portland cement is of extreme importance due to high levels of carbon dioxide emissions associated with its manufacturing process. This study investigates the effects of activating solution type, curing procedure, and source of fly ash in relation to the resulting compressive strength of fly ash-based geopolymer concrete. The fly ash-based geopolymer paste microstructure was observed and density, absorption and voids were measured. Two activating solutions were used: a) a mixture of sodium hydroxide, silica fume, and water; and b) a mixture of sodium hydroxide solution, sodium silicate, and water. Test results indicate that the resulting concrete has the potential for high compressive strength and the compressive strength is directly affected by the source of fly ash. Results further indicate that compressive strength is not significantly affected by the curing condition when silica fume is used in the activating solution in comparison to the use of sodium silicate.

Keywords: alkali-activated fly ash concrete, geopolymer concrete, early compressive strength, silica fume activating solution, sodium silicate activating solution

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¹FGC = Fly ash-based Geopolymer concrete

²FGC-silica fume = FGC with silica fume in the activating solution

³FGC-sodium silicate = FGC with sodium silicate in the activating solution

⁴SEM = Scanning Electron Microscopy

1. Introduction

A significant amount of concrete is used in construction around the world and Portland cement is one of the main constituents. Due to the very high temperatures required for the manufacture of Portland cement, vast amounts of energy are utilized for this ubiquitous construction material. It has been stated that the production of each ton of Portland cement releases approximately one ton of carbon dioxide [1], and that Portland cement industries contribute 5% to 7% of total worldwide CO₂ emissions [2]. In recent decades, a sustainable development has become a focus of scientists and engineers and, therefore, the quest for alternatives to this technology has accelerated.

One potential alternative to Portland cement based concrete is fly ash-based geopolymer concrete (FGC), which may have the potential to reduce Portland cement usage while mirroring the compressive strength and durability characteristics of Portland cement concrete [3,4]. Many studies have shown that FGC can demonstrate beneficial and diverse properties. For example, FGC has shown good resistance against acid and sulfate attack, high early age strength, and good performance in high temperatures [5-12]. It has been proven recently that FGC can achieve high early and final compressive strength in ambient curing condition, and good workability when additives are incorporated such as Portland cement, calcium hydroxide, or ground granulated blast furnace slag [13]. FGC is an inorganic polymer, which is produced by the reaction of alumino-silicate materials with alkaline solutions and the addition of conventional coarse and fine aggregate. FGC makes use of fly ash, which is a good source of alumino-silicate and is also a prevalent waste material. While the study described is focused on the use of fly ash, other waste materials such as blast furnace slag may also be utilized [14, 15]. FGC is generally agreed

to be less deleterious to the environment than Portland cement based concrete; however, more work to quantify this assertion is warranted.

A significant number of research studies have been conducted on FGC wherein sodium silicate was utilized in the activating solution [16, 17, 18, 19], as is also the case for alkali activated slag [20, 21]. In contrast, relatively few studies have investigated the combination of silica fume and sodium hydroxide as the activating solution [22]. Issues noted with the use of sodium silicate in the activating solution include relatively low workability and lower compressive strength when compared to conventional Portland cement based concrete, considered as 21MPa (3,000 psi) to 41 MPa (6,000 psi). Both activating solutions have the same major chemical components including Na_2O , and SiO_2 . However, the main differences are: 1) process of manufacturing, for instance sodium silicate solution is subjected to high temperature between 1100°C and 1200°C (2012°F and 2192°F), and then subjected to high pressure, and 2) the ratio of Si/Na in the activating solution where the ratio is higher in the silica fume based solution than the sodium silicate based solution. The strength of FGC has been noted to be improved when external heat in the range of 75°C (167°F) was applied early in the curing process. It is mentioned that the application of some external heat early in the curing process is feasible and relatively common for precast/prestressed concrete applications.

In addition to the materials utilized in the activating solution, the chemical composition of the fly ash itself varies considerably depending on the coal source and technological processes used, and these factors may significantly affect the resulting FGC properties [23]. Comparisons between different activating solutions and sources of fly ash are not widely available. This study aims to address some of the current gaps in knowledge by investigating the effects of activating

solution type, curing procedure, and source of fly ash in relation to the resulting compressive strength of FGC.

This paper compares compressive strength results obtained for FGC using either sodium silicate or silica fume in the activating solution. One significant finding is that the use of silica fume in the activating solution increases the compressive strength in comparison to the use of sodium silicate in the activating solution, potentially due to the higher silica concentration and smaller particle size of silica fume. The effect of different fly ash sources and curing conditions (samples stored either inside or outside the molds till the test day) are also investigated. The results indicate that the fly ash source has a significant effect on the resulting compressive strength. To gain further insight, the microstructure was observed to identify the major differences between fly ash sources by Scanning Electron Microscopy (SEM). To address and gain a better understanding of potential durability considerations, density, absorption and voids were measured in general conformance with ASTM (C 642-06) [24].

2. Materials and methods

In this section two experiments have been chosen from previous studies as first step. For FGC-silica fume, the mixture proportions followed Tempest et al. 2009 [22]. FGC-sodium silicate mixture proportions followed Lloyd and Rangan 2010 [18] due to high compressive strength and moderate workability. However, the mixture proportions were slightly changed to improve the compressive strength.

The materials used for fabrication of the FGC test specimens included fly ash (ASTM class F), activating solution (either sodium hydroxide mixed with silica fume or sodium hydroxide solution mixed with sodium silicate solution), and fine aggregate, water, and super plasticizer (Sika ViscoCrete 2100). Two fly ash sources were utilized in the investigation: a)

Belews Creek, from a power station in North Carolina, and b) Wateree Station, from a power station in South Carolina. The Wateree Station fly ash source was processed differently from the Belews Creek source, in that the Wateree Station source was subjected to a proprietary carbon burn out process. Chemical compositions of both fly ash sources are shown in Table 1. The activating solution used was either: a) silica fume (Sikacrete 950DP, densified powder silica fume), sodium hydroxide (97-98 purity, DudaDiesel), and water; or b) sodium silicate solution ($\text{NaO}_2 = 14.7\%$, $\text{SiO}_2 = 29.4\%$, and water = 55.9%, PQ Corporation), sodium hydroxide solution (14 M), and water. Local crushed coarse granite aggregates (Vulcan Materials) in a saturated surface dry condition and local fine aggregates (Glasscock) were used. The gradation of coarse and fine aggregate is provided in Table 2, and the proportions of the silica fume and sodium silicate based FGC are provided in Table 3.

X-ray Florence (XRF) and Thermal Gravimetric Analysis (TGA) were conducted to investigate the effect of fly ash source materials on FGC-silica fume at the Holcim (US), Inc. laboratory in Holly Hill, South Carolina. SEM observations were conducted on fly ash-based geopolymer silica fume paste samples in the SEM Center at University of South Carolina. Density, absorption and voids for FGC (silica fume and sodium silicate based) were measured according to ASTM (C 642-06) at 7 days after casting.

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Table 1: XRF chemical analysis of fly ash

Chemical analysis	Belews Creek Station, wt. %	Wateree Station wt. %
Silicon Dioxide	50.2	53.5
Aluminum Oxide	26.4	28.8
Iron Oxide	10.0	7.5
Sum of Silicon Dioxide, Aluminum Oxide	86.41	89.8
Calcium Oxide	4.3	1.6
Magnesium Oxide	1.3	0.8
Sulfur Trioxide	0.9	0.1
Loss on Ignition	2.0	3.1
Moisture Content	0.1	0.1
Total Chlorides	<0.002	-----
Available Alkalies as NaO ₂	0.7	0.8

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Table 2: Gradation of coarse and fine aggregate

Sieve (mm)	Coarse aggregate % passing	Fine aggregate % passing
16.0	100.0	100.0
12.5	99.5	100.0
9.50	85.3	99.8
4.75	28.8	99.5
2.36	5.5	97.9
1.18	1.3	90.4
0.43	0.7	37.2
0.30	0.7	20.0
0.15	0.5	1.6
Pan	0.0	0.0

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Table 3: Mixture proportions

Concrete type	Fly ash, kg/m ³ (lb/ft ³)	Water, kg/m ³ (lb/ft ³)	w/b ratio	Sodium hydroxide, kg/m ³ (lb/ft ³)	Silica fume, kg/m ³ (lb/ft ³)	Sodium silicate, kg/m ³ (lb/ft ³)	Coarse agg., kg/m ³ (lb/ft ³)	Fine agg., kg/m ³ (lb/ft ³)	SP% of fly ash
Mix 1: silica fume based activating solution	474 (29.6)	163 (10.2)	0.28	61.6 (3.8)	2.9 (46.2)	-	793 (49.5)	793 (49.5)	1.5
Mix 2: sodium silicate activating solution*	408 (25.5)		0.22	41 (2.6)	-	6.4 (103)	1110 (69.2)	739 (46.1)	1.5
Mix 3: sodium silicate activating solution	408 (25.5)	22.5 (1.4)	0.22	41 (2.6)	-	6.4 (103)	922.7 (57.6)	922.7 (57.6)	1.5

*Mix 2 is used in all the compressive strength results other than SS-W-OM-3

2.1 Activating solutions

For the silica fume based activating solution, sodium hydroxide flakes were dissolved in water and silica fume powder was then added and stirred for two minutes. The mixing of silica fume with sodium hydroxide and water resulted in an exothermic process (in excess of 80°C [176°F]). The activating solution was kept in a closed container in an oven at 75°C (167°F) for 12 hours to assure that the sodium hydroxide flakes and silica fume powder were completely dissolved. The water/binder ratio (w/b) was calculated as 28%. This ratio was calculated by dividing the water weight over summation of dried fly ash, sodium hydroxide and silica fume weight.

For the sodium silicate based activating solution, the sodium hydroxide solution (14 molarity concentration) was prepared by dissolving sodium hydroxide flakes in water and kept for at least 24 hours in ambient conditions. The sodium hydroxide and sodium silicate solution were then mixed together. The resulting solution was stored at ambient temperature for a period

of at least 24 hours, and then the extra water was added prior to mixing of activating solution with the dry ingredients (fly ash, fine aggregates, and coarse aggregates). Therefore, the water/binder (w/b) ratio of 22% was calculated by dividing total water weight (55.9% of weight of sodium silicate, the water of sodium hydroxide solution, and the extra water [22.5 kg/m³ (1.4 lb/ft³)] by weight of fly ash, sodium hydroxide flakes, 14.7% of sodium silicate for NaO₂, and 29.4% of sodium silicate for SiO₂ weight. It is worth noting that using higher w/b for FGC-sodium silicate will reduce the compressive strength drastically.

Mixing sodium silicate and sodium hydroxide solution does not result in significant exothermic heat. Since both sodium silicate and sodium hydroxide are in liquid state, external heat was not required for solution preparation, unlike the silica fume based activating solution described above.

2.2 Casting and curing

The dry ingredients (fly ash, fine aggregates, and coarse aggregates) were mixed for three minutes. The activating solution, which include the water, was then added to the dry mixture and mixed for five minutes. Cylinders with dimensions of 76 mm x 152 mm (3 in. x 6 in.) were cast by adding three lifts of concrete and rodding 60 times per lift with a 9.5 mm (0.3 in.) diameter rod [8]. The size of cylinders was chosen according to ACI 211.1-91 [20]. All specimens were externally vibrated for a period of 10 seconds [8]. For FGC-silica fume, the specimens were left in ambient condition for two days and then heated for a period of two days in an oven at 75 °C (167°F) [17]. For FGC-sodium silicate, the specimens were left for one day in ambient conditions and were then heated for a period of two days in the same oven at 75 °C (167 °F). The difference in aging time prior to placing in the oven is reported, but is not believed to be significant. Compressive strength testing was conducted at seven days after casting in all cases.

A total of forty FGC cylinders were mixed, cast, and conditioned. To enable the calculation of standard deviation four specimens of each type were prepared. One factor was altered while other factors were held constant [26]. The specimen nomenclature is described in the footnote to Table 4. Three variables were investigated: a) type of activating solution (either silica fume/sodium hydroxide/water or sodium silicate/sodium hydroxide/water); referred to as either ‘silica fume’ or ‘sodium silicate’ based activating solutions, SF or SS; b) source of fly ash (Belews Creek or Wateree Station), B or W; and c) curing condition (cured inside the plastic cylinder molds or cured outside the plastic cylinder molds, with mold removal performed just after the specimens were taken out of the oven), IM or OM. For example, SF-W-IM-1 indicates silica fume based activating solution, Wateree Station fly ash, cured inside the molds, patch number 1 of this type.

The test matrix contained two different sets of replicates as follows: a) silica fume based activating solution/Wateree Station fly ash/cured inside the molds (SF-W-IM), and b) sodium silicate based activating solution/Wateree Station fly ash/cured outside the molds (SS-W-OM). Replicate mixes are delineated with gray shading in Table 4. For the Wateree Station fly ash source, all variables of activating solution type and curing condition were thoroughly investigated. For the Belews Creek fly ash source, two combinations were studied (SF-B-IM and SS-B-OM).

Table 4: Matrix of test specimens

Specimen type	Activating solution		Fly ash source*		Curing condition		Number of specimens
	Silica fume	Sodium silicate	Wateree Station	Belews Creek	Inside the molds	Outside the molds	
SF-W-IM ⁵ -1	X		X		X		4
SF-W-IM-2	X		X		X		4
SF-W-IM-3	X		X		X		4
SF-W-OM ⁶	X		X			X	4
SS-W-OM ⁷ -1		X	X			X	4
SS-W-OM-2		X	X			X	4
SS-W-OM-3**		X	X			X	4
SF-B-IM ⁸	X			X	X		4
SS-W-IM ⁹ -1		X	X		X		4
SS-B-OM ¹⁰		X		X		X	4

*both fly ash sources Type F

**Mixture No. 3 (Table 3)

Note: Shaded cells indicate replicate specimens

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SF= silica fume based activating solution

SS= sodium silicate based activating solution

W= Wateree fly ash

B= Belews Creek fly ash

IM= cured inside the molds

OM= cured outside the molds

3. Results and discussion

Results of the compressive strength testing are shown in Table 5, ranked in descending order of compressive strength. The Wateree Station fly ash source in combination with the silica fume based activating solution resulted in the highest values of compressive strength regardless of the curing condition, with an average result of 105.0 MPa (15,240 psi) when curing was

⁵ SF-W-IM= silica fume based activating solution/Wateree fly ash/Inside the molds

⁶ SF-W-OM= silica fume based activating solution /Wateree fly ash/Outside the molds

⁷ SS-W-OM= sodium silicate based activating solution /Wateree fly ash/Outside the molds

⁸ SF-B-IM= silica fume based activating solution /Belews Creek fly ash/Inside the molds

⁹ SS-W-IM= sodium silicate based activating solution /Wateree fly ash/Inside the molds

¹⁰ SS-B-OM= sodium silicate based activating solution /Belews Creek fly ash/Outside the molds

performed in the molds. The compressive strength results for the silica fume/Wateree Station/in molds combination were quite repeatable, with a difference of 2.1 MPa (351 psi) between the highest and lowest results (within approximately 2% of the average result). To enable comparisons between the different specimens, the highest compressive strength result [106.0 MPa (15,380 psi)] was chosen as a reference. Other results are reported as a percent deviation from that baseline in the far right column of Table 5. A discussion of the effect of the type of activating solution, the curing condition, and the fly ash source, is provided below.

Table 5: Experimental results

Specimen type	Activating solution	Fly ash source	Curing condition	Average* compressive strength at 7 days, MPa (psi)	Standard deviation, MPa (psi)	Deviation below reference (%)
SF-W-IM-1	Silica fume	Wateree Station	Inside the molds	106.0 (15,380)	4.0 (580)	0.0
SF-W-IM-2	Silica fume	Wateree Station	Inside the molds	105.5 (15,300)	4.4 (635)	0.1
SF-W-IM-3	Silica fume	Wateree Station	Inside the molds	103.8 (15,050)	2.4 (350)	0.1
SF-W-OM	Silica fume	Wateree Station	Outside the molds	93.8 (13,600)	2.8 (410)	12
SS-W-OM-1	Sodium silicate	Wateree Station	Outside the molds	60.7 (8,800)	2.6 (380)	43
SS-W-OM-2	Sodium silicate	Wateree Station	Outside the molds	59.5 (8,630)	2.9 (425)	44
SS-W-OM-3**	Sodium silicate	Wateree Station	Outside the molds	56.7 (8,210)	1.9 (280)	47
SF-B-IM-1	Silica fume	Belews Creek	Inside the molds	43.8 (6,350)	1.9 (285)	59
SS-W-IM-1	Sodium silicate	Wateree Station	Inside the molds	38.5 (5,580)	2.6 (380)	64
SS-B-OM	Sodium silicate	Belws Creek	Outside the molds	15.2 (2,200)	1.4 (210)	86

*average of four specimens

**Mixture No. 3 (Table 3)

Note: Shaded cells indicate replicate specimens

SF= silica fume based activating solution

SS= sodium silicate based activating solution

W= Wateree fly ash

B= Belews Creek fly ash

IM= cured inside the molds

OM= cured outside the molds

3.1 Effect of activating solution type

The effect of different activating solution types is apparent by comparing SF-W-IM-1, (silica fume based activating solution) 106.0 MPa [15,380 psi]; and SS-W-IM-1 (sodium silicate based activating solution, 38.5 MPa [5,580 psi]) in Table 5. The results are shown graphically in Figure 1. The comparison shows that the compressive strength is 64% lower when sodium silicate was used in place of silica fume in the activating solution. This is attributed to the fact that geopolymer framework in fly ash-based geopolymers consists of bonds between oxygen and silica; oxygen, silica, alumina; and oxygen, silica, alumina, and iron. The availability of readily available silica to form the geopolymer chains is necessary for strong bonds within the polymer chains. The total weight of Si/Na ratio of FGC-silica fume is 52%, while the ratio for FGC-sodium silicate is 43%. This difference in the Si/Na weight ratio may contribute to the compressive strength. In addition, the total weight ratios of Na/H₂O of FGC-silica fume and FGC-sodium silicate are 21%, and 42% respectively. In conclusion, the increase in the Si/Na ratio and the reduction in the Na/H₂O ratio may improve the compressive strength of fly ash-based geopolymer concrete. As shown in Table 3, water/binder ratio are higher in the FGC-silica fume than FGC-sodium silicate, which leads to conclude that the water/binder ratio difference does not explain the reason of high compressive strength in the FGC-silica fume samples. In Mix 3 (SS-W-OM-3), which is used to identify effect of aggregate on the compressive strength, as shown in Table 3, the course/fine aggregate in the FGC-sodium silicate was changed to 1:1 to investigate effect of gravel ratio. The difference in compressive strength of specimens cast using Mix 2 (SS-W-OM-1) and Mix 3 (SS-W-OM-3) is approximately 7% which shows that no significant difference was observed when the aggregate ratio was modified.

Fig. 1 Effect of activating solution type (comparing SF-W-IM-1 to specimen SS-W-IM of Table 5),
1 MPa = 145.038 psi

3.2 Effect of curing condition

The Wateree fly ash source was used for all curing condition comparisons. The effect of different curing conditions on FGC-silica fume is apparent by comparing SF-W-IM-1 (cured in molds; 106.0 MPa [15,380 psi]) and SF-W-OM (cured outside of molds; 93.8 MPa [13,600 psi]) in Table 5. The results are shown graphically in Figure 2. The comparison shows that the compressive strength is 12% lower when the specimens were cured outside the molds. An opposite trend was observed for the specimens of FGC-sodium silicate. By comparing SS-W-OM-1 (cured outside of molds; 60.7 MPa [8,800 psi]) and SS-W-IM-1 (cured in molds; 38.5 MPa [5,580 psi]) in Table 5 (shown graphically in Figure 3), it can be seen that curing in the molds resulted in a 37% reduction in compressive strength.

The reason for slight difference in the FGC-silica fume results is attributed to the high rate of polymerization reaction; therefore, the compressive strength is only slightly affected when specimens are cured outside the molds. For FGC-sodium silicate, the degree of polymerization may be higher, and the significant difference in compressive strength may be

attributed to an expansion which may produce micro-cracking if the sample is kept in a constrained container. Further studies are recommended to aid in the explanation of differences in compressive strength when curing conditions are changed.

Fig. 2 Effect of curing condition on FGC-silica fume (comparing SF-W-IM-1 to SF-W-OM of Table 5), 1MPa = 145.038 psi

Fig. 3 Effect of curing on FGC-sodium silicate (comparing SS-W-IM-1 to SS-W-OM of Table 5), 1MPa = 145.038 psi

3.3 Effect of fly ash source

The effect of different fly ash sources on the resulting compressive strength of FGC-silica fume is apparent by comparing SF-W-IM-1 through SF-W-IM-3 (Wateree Station fly ash source; average of all three specimens = 105.1 MPa [15,240 psi]) and SF-B-IM-1 (Belews Creek fly ash source; 43.8 MPa [6,350 psi]) in Table 5. The comparison shows that the compressive strength increased by 58% when the Wateree Station fly ash source was utilized. This significant increase in compressive strength associated with the Wateree Station fly ash source was not expected and the reason for this dramatic increase is not entirely clear. It is noted that the Wateree Station source was subjected to a carbon burn out process while the Belews Creek source was not. This unexpected increase in compressive strength prompted further chemical and petrographic analysis, SEM observations, as well as absorption and void space ASTM (642-06) testing, as described further below. The results of the comparison of SF-W-IM and SF-B-IM are shown graphically in Figure 4.

Fig. 4 Effect of fly ash source (comparing SF-W-IM-1 to SF-B-IM-1 of Table 5),
1MPa = 145.038 psi

3.3.1 X-Ray Florescence (XRF) and Thermal Gravimetric Analysis (TGA)

The chemical and physical characteristics of FGC-silica fume made using different fly ash sources, the Wateree Station fly ash (SF-W-IM-1, Table 5) and the Belews Creek Station fly ash (SF-B-IM-1, Table 5), were further investigated in an attempt to understand the difference in compressive strength.

The chemical differences between the two specimens (SF-W-IM-1 and SF-B-IM-1) were investigated by conducting x-ray florescence (XRF) as shown in Table 6 using fused bead analysis. In addition, thermal gravimetric analysis (TGA) was used to look at powdered paste samples prepared using both fly ashes in combination with the entire binder system (rather than just the fly ash powder component) to examine the total reaction products. The XRF analysis method was used for chemical analysis of the fly ash, while the TGA method used coal analysis for the fly ash to focus on the determination of carbon and sulfur.

The results of XRF showed that the binder system containing the Wateree Station fly ash did have 4.58% more silica dioxide (SiO_2) and 2.54% more aluminum oxide (Al_2O_3) per weight of binder than the binder system containing the Belews Creek fly ash. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of both fly ash sources were almost the same where the Wateree Station fly ash binder system had a ratio of 2.19% while the Belews Creek binder system had a ratio of 2.22%. This indicates that the ratios were fairly consistent, but the Wateree fly ash binder system had more SiO_2 and Al_2O_3 to form reaction products when introduced to the sodium hydroxide (NaOH) and silica fume activator in the form of Si-O and Si-O-Al-O- polymer chains. The calcium oxide (CaO) and sulfur in the form of (SO_3) were also higher in the Belews Creek binder system, which are not considered in the reaction products contributing to compressive strength and could be considered as dilution products by reducing the total amount of SiO_2 and Al_2O_3 available when compared to

the Wateree fly ash. This is only a theory, but considering that there is less SiO_2 and Al_2O_3 in the Belews Creek ash to form reaction products, it could contribute to some of the lower compressive strength results.

Both powder paste samples did show very high alkali levels with both showing levels at 8.7%, but this is expected due to the use of sodium hydroxide (NaOH) as part of the activating solution. However, the high alkali levels reported in the XRF analysis are important to mention due to the potential of alkali silica reactivity when utilized in some concrete systems.

TGA was used to determine the differences in SO_3 and carbon (C) content between the two samples. In terms of dilution factors the results showed that the Wateree Station based powdered paste had a higher content of both compounds, but the percentages of these compounds in the systems are very small and probably have little to do with the compressive strength differences when used in concrete. However, the higher carbon content in the Wateree Station based paste is probably the reason for the darker color seen in both the paste and concrete samples.

The concrete samples investigated were from two broken 75 mm x 150 mm (3 in. x 6 in.) cylinders, as shown in Figure 5, that were previously tested for compressive strength. One was from concrete made using the Wateree Station fly ash source which had a compressive strength of about 106 MPa (15,300 psi), SF-W-IM-1, and the other from concrete made using the Belews Creek fly ash source resulting in compressive strength of about 43 MPa (6,350 psi), SF-B-IM. It was observed that the paste fraction of the Wateree fly ash was darker in color. Both samples were cut along the longitudinal axis and polished for petrographic analysis with three random areas selected for microscopic examination as shown in Figure 6.

Observations noted were that the coarse aggregate in the Belews Creek samples had larger aggregate particles and may have been from a different aggregate source or may have been blended in with the same aggregate source as the Wateree Station sample, but the differences in the coarse aggregate did not appear to have contributed to the differences in the compressive strength due to the sharp clean aggregate fractures along the failure planes of both samples.

The paste density appeared similar in both concretes and was noted as being very dense when compared to conventional concretes, but the paste uniformity seemed to look better in the higher strength concrete [SF-W-IM-1]. The paste contrast did look sharper and less muted in the Wateree Station sample, which may suggest a higher percentage of glass dissolution that took place during the chemical process between the fly ash and the activating solution.

The overall hardened air volume and void size looks slightly larger in the Belews Creek sample, but both concrete samples had very low air contents, in the range of 1% or less. The differences in air content in combination with differences in glass dissolution and chemical dilution factors of non-reactive materials in the fly ashes may have caused the differences in compressive strength. However, additional research is warranted to better understand the reasons of the compressive strength differences.

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Table 6: XRF chemical analysis of paste

Compound	Wateree Station (SF-W-IM-1) Sample wt.%	Belews Creek Station SF-B-IM-1 (Sample) wt.%
Silicon Dioxide	55.4	50.9
Aluminum Oxide	25.4	22.9
Iron Oxide	4.6	7.7
Calcium Oxide	0.6	3.9
Magnesium Oxide	0.6	1.0
Sulfur Trioxide	0.1	0.6
Sodium Dioxide	7.4	7.0
Potassium Oxide	2.1	2.7
Total Alkali	8.7	8.7
Phosphate (P2O5)	0.1	0.3
Titanium Dioxide	1.1	1.0
Manganese Oxide	0.1	0.1

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Fig. 5 Prepared vertical test sections of FGC-silica fume, 1MPa = 145.038 psi

Fig. 6 Micrograph images of FGC-silica fume, 1MPa = 145.038 psi

3.3.2 Scanning Electron Microscopy (SEM) observations

To investigate the microstructure of FGC-silica fume and the differences when different fly ash sources were used, two fly ash-based geopolymer pastes were prepared. The fly ash-based geopolymer paste samples were cast at the same time and environment according to the procedure explained in the materials section above. The activating solution, a combination of silica fume, sodium hydroxide and water, was prepared as described in the material section. It was then mixed with one of the two different fly ash sources (Wateree Station or Belews Creek). The two paste samples were kept for two days at ambient temperature, and were then heated for two days at 75°C (167°F). The SEM observations were conducted in the microscopy center at the

University of South Carolina. The age of the fly ash-based geopolymer paste samples was 7 days when the SEM observations were conducted. Figure 7.A shows that the Wateree Station fly ash paste is completely dissolved and reacted with the activating solution. Comparing with the Belews Creek fly ash paste sample shown in Figure 7.B, the Wateree sample appears free of voids and is relatively dense. On the other hand, for fly ash-based geopolymer paste with Belews Creek fly ash, Figure 7.D shows that there is some fly ash that has not yet reacted compared with the Wateree sample shown in Figure 7.C. The unreacted fly ash in the Belews Creek sample may have resulted from two reasons: 1) Particle size distribution, shown in Figure 8, where Wateree Station fly ash is finer than Belews Creek fly ash. The average particles size for Wateree and Belews Creek fly ash is 16.2 and 20.3 μm respectively with difference in value of 26%. This leads to a higher polymerization rate due to large surface area; 2) Some of the Belews Creek fly ash particles were isolated from the activating solution (within cenospheres), which may delay the polymerization process. Therefore, it can be deduced that the fly ash source not only affects the reaction between the activating solution and fly ash, which may reduce the compressive strength of FGC, it may also affect the durability of resulting FGC-silica fume concrete due to high apparent voids. As shown in the figures, there is a significant difference in the number of voids when the fly ash source was changed.

Fig. 7 SEM observation: A) Wateree fly ash paste, B) Belews Creek fly ash paste, C) Wateree fly ash paste at higher magnification, and D) Belews Creek fly ash paste at higher magnification

Fig. 8 Fly ash particle size distribution

3.3.3 Absorption and void space results (ASTM C 642-06)

The absorption and void space of FGC specimens fabricated with two different activating solutions (silica fume/sodium hydroxide or sodium silicate/sodium hydroxide) and two different fly ash sources, Wateree Station and Belew's Creek, were investigated. New samples were cast using combinations of the two factors as shown in Table 7. The samples were cast and cured following the same procedures described previously. Four samples were tested for each specimen. The age of the concrete was 7 days in all cases. The main purpose of this test was to investigate the effect of different fly ash sources on the absorption, density and voids of FGC-silica fume and FGC-sodium silicate. The relationship between the compressive strength and the total permeable voids space (ASTM C 642-06) was also studied.

As shown in Table 7 and Figure 9, specimens with Belew's Creek fly ash had higher absorption and volume of permeable pore space in both FGC activating solutions. FGC with Wateree Station fly ash has a lower volume of permeable pore space in comparison with results of conventional concrete found in the literature [27]. Figure 10 shows a clear correlation between volume of permeable pore space and compressive strength. Considering the same activating solution, when the rate of absorption and volume of permeable pore space increase the associated compressive strength decreases. In addition, the bulk and apparent density increased when Wateree Station fly ash was used regardless of the activating solution type. This test shows that FGC with Wateree Station fly ash is denser than FGC with Belew's Creek fly ash, i.e. fewer and/or smaller voids exist in the Wateree Station fly ash FGC. This observation is in agreement with, and confirms, the reported SEM observations.

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Table 7: Sample description and ASTM 642-06 results

Specimen type	Activating solution	Fly ash source	Bulk density* (dry), g/cm ³ (lb/ft ³)	Apparent density* g/cm ³ (lb/ft ³)	Absorption after immersion*, %	Volume of permeable pore space*, %	Compressive strength*, MPa (psi)
SF-W-IM-4	Silica fume	Wateree Station	2.19 (137)	2.48 (155)	5.0	11.7	106.1 (15,390)
SF-B-IM-2	Silica fume	Belews Creek	2.10 (131)	2.46 (153)	6.1	14.6	43.9 (6,360)
SS-W-IM-2	Sodium silicate	Wateree Station	2.23 (139)	2.49 (155)	4.3	10.0	60.6 (8,790)
SS-B-IM	Sodium silicate	Belews Creek	2.16 (135)	2.46 (154)	5.3	12.2	17.2 (2,500)

*average of four specimens

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Fig. 9 Volume of permeable pore space and absorption after immersion

Fig. 10 Volume of permeable voids space and compressive strength correlation,
1MPa = 145.038 psi

4. Conclusions

1. A significantly high early compressive strength was achieved (around 105.1 MPa [15,240 psi]) with fly ash-based geopolymer concrete (FGC) using Type F fly ash and silica fume activating solution. The cementitious materials content was 100% fly ash (no Portland cement). This shows the promise of developing and using this alternative concrete to replace ordinary Portland cement concrete. However, the use of heat during the curing period may, for the near future, limit applications of this material to precast concrete.
2. The use of silica fume based activating solution resulted in higher compressive strength values as compared to similar specimens cast using sodium silicate based activating solution.
3. Curing conditions (cured inside or outside the molds) did not have a significant effect on the compressive strength when silica fume was used in the activating solution. For these specimens, curing outside of the molds resulted in lower compressive strength.

The opposite trend was observed when sodium silicate was used in the activating solution, where significantly higher compressive strength values were achieved in specimens cured outside the molds.

4. The use of different fly ash sources (Wateree Station fly ash versus Belews Creek fly ash) had a significant impact on the compressive strength of fly ash-based geopolymer concrete (FGC) due to particle size distribution difference and isolated fly ash particles (entrapped within cenospheres), which led to significant differences in the microstructure as well.
5. Samples fabricated with the Wateree Station fly ash source resulted in less absorption after immersion and volume of permeable voids space than samples fabricated with the Belews Creek fly ash source.

It is noted that this study did not investigate potential concrete material degradation mechanisms associated with the use of external heat curing, such as delayed ettringite formation (DEF), or the high alkalinity of the concrete, such as alkali-silica reaction (ASR). However, DEF in FGC with fly ash Type F is less likely to occur because the calcium oxide component is low (around 4% of the total material). If fly ash Type C is used, DEF may affect the sustainability of the concrete. The high alkalinity of FGC promotes ASR degradation; therefore, only aggregates known to have low propensity for reactivity should be considered for use in FGC.

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