COMPRESSIVE STRENGTH VARIABILITY OF BROWN COAL FLY ASH GEOPOLYMER CONCRETE

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Abstract

The use of Fly Ash (FA) as an alternative binder material to Ordinary Portland Cement (OPC) is well established, with class F FA the most commonly used in the synthesis of this alkali-activated binder at present. ASTM C618 classifies FA as class F produced from anthracite and bituminous and class C from lignite and sub-bituminous coals. In Australia, Victoria FA is produced from lignite known as Brown Coal (BC), but due to the chemical composition cannot categorize as class C. Recent studies have shown the viability of using 100% BC FA as the binder to create alkali activated geopolymer concrete. A previous study using Victoria BC FA for geopolymer concrete provided strength of more than 40MPa which is comparable to class F geopolymer and OPC specimens. The activation process of geopolymer concrete varies remarkably from PC concrete, due to the activation of the aluminosilicate by high concentration alkali. Therefore, the durability of geopolymer concrete may possibly be different to OPC concrete. This paper reports on a research project investigating compressive strength variability that could, in turn, affect the durability characteristic of the BC FA geopolymer concrete for use in the construction industry.

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Keywords: fly ash, brown coal, geopolymer concrete, variability, compressive strength

1. INTRODUCTION

Environmental concerns have been raised regarding the energy consumption and the emission of CO_2 in the production of Portland cement as the main binder material in concrete [1, 2]. While other concerns have highlighted the use of coal as a primary energy source in the world. The use of coal releases FA as a by-product material, some of which becomes environmental waste [3].

In order to address these environmental issues, the use of waste products such as FA as partial replacement materials for OPC have become well established [1, 4, 5]. These materials give both an environmental benefit, being waste materials and also provide improved performance for the concrete produced, especially in the area of durability.

ASTM C618 [6] defines FA into 2 classes, class F and class C. Class F FA is produced from burning anthracite and bituminous coals, while class C FA is produced from subbituminous coals and lignite. Both have pozzolanic properties, and in addition to that, class C FA also has some cementitious properties. At present only class F FA may be used as a partial replacement material for Portland cement, while class C FA cannot be used as a replacement material for OPC, due to the chemical composition adversely affecting the properties of the concrete produced.

Australia's 2008 recoverable lignite (low-rank coal) also known as BC is estimated to be 37.2 giga tonnes, all of which is located in La Trobe Valley, Victoria [7]. Victoria annually produces more than 500 kilo tonnes of combined BC FA and bottom ash. There are three sources of BC FA in Victoria, Loy Yang, Hazelwood and Yallourn power station, in the La Trobe valley. Each FA has a unique composition. So far little research has been undertaken on the feasibility of using BC FA as a waste product [8, 9]. The BC FA is not used a partial replacement material due to the CaO content and the very high SO₃ content. As such there is no commercial use of the material in the construction industry, with the majority of the material being sent to landfill at present.

1.1 Geopolymer Concrete

Recent research has shown the feasibility of using class F FA as 100% of the binder to create alkali-activated concrete, known as geopolymer concrete [10]. The activation process for geopolymer concretes is due to the activation of the aluminosilicates by high concentration alkali [11] rather than the activation of the FA by the $Ca(OH)_2$ produced by the hydration of the OP cement [12]. To date research has focused on the use of class F FA, which has a high aluminosilicates content, which is required for the activation process. Therefore, if the composition of the aluminosilicates in the class C FA is sufficient it may be feasible to use them to produce geopolymer concrete. The potential demonstrated for class C FA could also be applied to BC FA that is a by-product from the same source. This potential use of BC FA could result in utilization of a widespread industrial by-product from coal burning power stations, which is presently dumped into the environment. A previous study at RMIT on geopolymer concrete using Loy Yang BC FA as 100% replacement of OPC

demonstrated compressive strength comparable to those obtained from OPC concrete [13]. The results were indicative that Loy Yang BC FA geopolymer concrete can produce compressive strengths acceptable for use in the construction industry.

Good performance service and durability is a major factor for success of concrete as a construction material [14]. Durability of concrete is the ability to resist weathering action, chemical attack, abrasion, or any process of deterioration as a result of a variety of physical and chemical processes. Further investigation is required to determine the mechanical properties and durability characteristics of the geopolymer concrete prior to use in the construction industry.

The paper reports an ongoing investigation of compressive strength variability that could affected the durability characteristic of Loy Yang, Victoria BC FA geopolymer concrete.

2. MATERIALS AND METHODS

2.1 Materials

The FA used in this study came from Loy Yang Power Station in the La Trobe Valley, Victoria, Australia. Table 1 shows chemical composition of the BC FA supplied and chemical composition from a study previously reported in 1993 [15].

Table 1: Chemical Composition of Loy Yang BC FA

Oxide (%)	Current Study	Ref [15]
SiO ₂	47.52	60.4
Al_2O_3	17.29	13.3
Fe ₂ O ₃	5.98	8.5
CaO	2.25	1.0
MgO	4.63	2.2
K ₂ O	0.50	1.2
Na ₂ O	6.26	2.1
TiO ₂	1.26	1.7
P_2O_5	0.74	
SO ₃	13.03	3.4
Cl		<0.1
Cl ₂ O	0.44	
Mn ₂ O	0.10	
LOI		7.6

A 15 M sodium hydroxide solution (with composition of 37.5% NaOH and 62.5% water) was used together with sodium silicate (Na₂SiO₃) with a 2.00 ratio liquid sodium silicate (Na₂O = 14.7%, SiO₂ = 29.4% and 55.90% water) of 1.52 g/cc density.

2.2 Mix Design

The mix design used in this study was based on the best mix from an earlier pilot study of geopolymer mortar [16]. Table

2 shows the mix proportions and mass ratios of mortar specimen from the pilot study.

A portion of fine aggregate (sand) was substituted by a combination of sand and aggregates. The aggregates used for the mix was a combination of 43% of sand, 38% of 10mm aggregate and 19% of 7mm aggregate (Table 3). Those percentages of combined aggregates were adopted from previous research at RMIT in the development of Class F FA geopolymer concrete with the same source of aggregates [17]. The fine aggregate was uncrushed sand and the coarse aggregates were crushed basalt aggregates. The aggregate moisture condition was oven dried aggregates.

Table 2: Mortar Mix Proportion and Mass Ratio

Mass Proportion (kg)							
BC FA	Sand	l	Na ₂ SiO ₃		NaOH		
0.279	1.677		0.363		0.021		
Mass Ratio							
SiO ₂ /Na ₂ O	D Liquid/Solid FA wt%						
3.11		0.102		11.9	94		

 Table 3: BC FA Geopolymer Concrete Mix Proportion

Mass (kg)							
	Aggregates Na ₂ SiO NaO						
БС ГА	Sand	7-mm	10-mm	3	Н		
0.279	0.721	0.319	0.637	0.363	0.021		

2.3 Preparation of BC FA Geopolymer Concrete

The casting procedure was adopted from the previous geopolymer study at RMIT [17]. The BC FA geopolymer concrete mixing was performed using a 25-litre mixer. Directly after mixing the concrete was placed in 100 x 100 x 100 mm cubic molds. The specimens were compacted with two-layer placing and tamping, and placed on a vibration table for 30 seconds. The specimens were left for 24 hours at room temperature and then covered to prevent moisture loss and put in the oven pre-heated at 120°C for 10 hours. The specimens were left to cool at room temperature before being de-molded. The specimens were kept at room temperature prior to testing. Elevated curing has been shown to assist the chemical reactions that occurs in geopolymer concrete [12, 18]. An earlier study validated a curing temperature of 120°C as suitable for La Trobe Valley BC FA [19]. A curing temperature of 120°C resulted in a significantly higher compressive strength for BC FA mortar specimens than a curing temperature of 80°C.

Table 4: Group of Casting, Mass and Volume

Group	Mass (kg)	Volume (litre)
1	26.881	11
2	53.884	22.05
3	61.581	25.2
4	35.922	14.7
5	34.488	15.75
6	29.569	12.1

A total of 6 mixes were cast. These specimens were intended for both compressive strength and durability tests and as such were of different volumes (mass). Table 4 lists the total mass and volume per mix. Each mix was produced from the same batch of BC FA supplied from Loy Yang power station directly from the precipitator units with no pre-treatment. Each mix consisted of $3 \times 100 \text{ mm}^3$ cubes for compressive strength tests at 28 days and a range of different size and shape specimens for durability tests.

3. COMPRESSIVE STRENGTH RESULTS

Compressive strength measurements were performed on a Universal Testing Machine and MTS machine in accordance with BS EN 12390-3. Three cubes were tested for each data point.

A total of 6 groups of samples were tested for compressive strength, Table 5. Group 1 was tested at 7, 28 and 91 days, groups 2-6 were tested at 28 days.

 Table 5: BC FA Geopolymer Compressive Strength Results

Group	Compressive Strength - MPa Mean(SD)			
-	7days	28days	91days	
1	44.95(1.98)	43.81(4.31)	42.62(6.25)	
2		29.38(6.62)		
3		23.76(2.73)		
4		7.21(2.35)		
5		31.41(7.72)		
6		13.29(4.43)		

4. DISCUSSION AND CONCLUSION

The compressive strength results (Table 5) show a large range in strength, from 43.81MPa (group 1) to 7.21MPa (group 4) at 28 days. The results indicate a wide variation in the quality of the material. It is hypothesized that this variation may be due to BC FA being supplied as a raw material, with no pretreatment and refining, as undertaken for commercial Class F FA. A significant variation in the chemical composition was observed compared to that reported by other authors [15] despite the materials being from the same source, Table 1.

Oxide	Sample				
(%)	А	В	С	D	Е
SiO ₂	51.92	49.66	54.16	52.96	67.53
Al_2O_3	12.42	13.54	13.00	12.69	8.53
Fe ₂ O ₃	6.84	7.05	7.01	7.06	4.54
CaO	2.47	2.57	2.34	2.35	1.23
MgO	4.13	4.34	3.64	4.06	2.28
K ₂ O	0.51	0.46	0.48	0.48	0.51
Na ₂ O	5.24	5.29	4.75	5.50	3.63
TiO ₂	1.23	1.17	1.27	1.21	1.15
P_2O_5	0.71	0.58	0.49	0.47	0.82
SO ₃	13.86	14.73	12.43	12.42	9.09
Cl ₂ O	0.54	0.51	0.38	0.73	0.56

Table 6: Composition Variation of Loy Yang BC FA

Mn ₂ O	0.15	0.09	0.08	0.10	0.14

Therefore, additional chemical analysis was done to determine the inherent variation in the material. Table 6 shows chemical composition variation of 5 additional samples taken from the same batch as used in the compressive strength tests reported in Table 5. The data shows significant variations with the SiO₂ content varying from 47.52 % (current study; Table 1) to 67.53 % (Table 6, Sample E), the Al₂O₃ content varying from 17.29 % (current study, Table 1) to 8.53 % (Table 6, Sample E) and the total SiO₂ + Al₂O₃ content varying from 76.06 % (Table 6, Sample E) to 63.2 % (Table 6, Sample B).



Fig. 1 Strength vs Alkali Modulus (SiO₂/Na₂O) observed in earlier studies [20].

The activator modulus (Ms) is the mass ratio of the SiO₂ to Na₂O in the alkaline activator (NaOH and Na₂SiO₃ solutions). The modified activator modulus (Msm) is calculated to include the silicon dioxide (SiO₂) and sodium oxide (Na₂O) content from the BC FA. Earlier studies has indicated the important role of alkali modulus SiO₂/Na₂O in determining compressive strength of geopolymer mortar [16, 20]. Figure 1 shows the influence of the alkali modulus (SiO₂/Na₂O) on the 7days strength of the Loy Yang BC FA geopolymer mortar [20]. The alkali modulus of the graph is a modified activator modulus (Msm). It shows the small range of mix compositions for which compressive strength above 40MPa can be achieved. The optimum compressive strength of 56MPa was obtained with an alkali modulus 3.11.

Sampla	Activator Modulus		
Sample	Ms	Msm	
Ref [13]	1.795	3.112	
А	1.795	3.398	
В	1.795	3.306	
С	1.795	3.548	
D	1.795	3.404	
Е	1.795	4.245	

Table 7: Alkali Modulus of different chemical composition

Using the chemical composition variation of Loy Yang BC FA (Table 6), the Ms and Msm were calculated from the mix proportion BC FA geopolymer concrete (Table 2 and

3). Table 7 illustrates how the inherent variations in the material gave substantial differences in alkali modulus Msm. The initial trial study sample [13] had the lowest Msm of all the samples, while all the other samples have higher values. The higher values of Msm are in the region corresponding to compressive strengths for a mortar of less than 30MPa (Figure 1), correlating with the values actually observed for the concretes.

These results indicate that the compressive strength of the concrete is highly dependent on the chemical composition (and hence Msm) of the BC FA. As such the quality of the BC FA used in the manufacture is critical to the quality of the concrete and that refining of the BC FA may be necessary prior to adoption as a geopolymer concrete material.

It is further hypothesized that the increase in volume of the sample sizes has contributed to the variations in strength observed. Table 4 shows the smallest mix, group 1, provided the highest compressive strength of 42-44MPa. An initial trial study on small batch Loy Yang BC FA geopolymer concrete gave results ranging from 40-60MPa, Table 8 [13]. Mix 1 used saturated surface dry aggregates, and mix 2 used oven dried aggregates. Both mixes in Table 8 had the same mass (26.881 kg) and volume (11 litres), similar to group 1 in Table 4. The results both show higher compressive strengths are achieved for lower volumes of mix.

 Table 8: BC FA Geopolymer Compressive Strength Results

 obtained in earlier study [13]

BC FA	Compressive Strength - MPa					
GC	Mean(SD)					
Mir 1	3days	7days	28days			
IVIIX I	45.98(1.65)	43.60(4.26)	40.59(8.00)			
Mir 2	7days	56days	91days			
IVIIX Z	59.59(3.49)	52.08(3.88)	60.38(0.46)			

Mixing of the material is an important factor in enabling efficient dissolution of the FA particles. The increased volumes may also have led to inefficiencies in the mixing, which further contribute to the variations in strength.

5. CONCLUDING REMARKS

The sample of BC FA geopolymer concrete of this paper were intended to use for durability testing of Loy Yang BC FA geopolymer concrete. However the compressive strength results demonstrated significant variations. Analysis of the chemical compositions of the BC FA observed a wide range of silicate and aluminate concentrations, which is attributed as the primary reason for this variation. The lack of pretreatment of the BC FA, which is an untreated waste material, is hypothesized as the cause of the variation observed. The results indicate that further treatment of the BC FA may be necessary prior to adoption as a geopolymer concrete material. Durability testing of the BC FA geopolymer concrete such as air and water permeability test, carbonation, salt ponding test, rapid chloride permeability test will be continued once this issue has been addressed.

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