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Blended Low Calcium Fly Ash Gepolymer Concrete – Environment Friendly Construction Material

D S Cheema[1 +], N Lloyd [2]

[1]Curtin University, Perth, Western Australia
[2]Curtin University, Perth, Western Australia

Abstract. Alkali activated low fly ash-based geopolymer concrete (LCFG) is an environment friendly construction material because of its zero cement content, however its rapid strength gain mechanism is sensitive to heat curing as per past research studies. Blended LCFG concrete with small proportion of slag is more aligned to conventional Ordinary Port Land Cement (OPC) concrete for initial strength gain under ambient curing conditions and can be potential construction material. Blended LCFG concrete binder being by-products from coal fired power station and iron extraction process offer considerable saving of CO_2 emission which otherwise is probable with OPC production due to its intensive energy requirements. This paper presents the findings of blended LCFG concrete and LCFG concrete and its potential replacement scenarios to OPC concrete.

Keywords: Alkali activation, Low fly ash-based geopolymer (LCFG) concrete and Blended LCFG

1. Introduction

An estimated worldwide use of concrete is in the order of 15 billion tonnes per annum and is far exceeding than the use of coal, oil and steel. Concrete manufacturers are the fourth largest contributors to man –made global carbon emission trailing behind oil, coal and natural gas [1]. OPC is the dominant source of carbon emission in OPC concrete, that is, production of one ton of OPC produces approximately one ton of CO_2 emission [2], [3]. As LCFG binders are alkali activated, its one component is NaOH, which is produced from chloro- alkali process in which the primary purpose is to produce chlorine and secondary purpose is to make NAOH. If the CO_2 emission resulting from the process is taken on the basis of 50-50 split, CO_2 emission associated with one ton production of NaOH will be 0.5 ton [1]. But only a meagre quantity of 12kg is required in the manufacturing of one cubic meter of geopolymer concrete, compared to 350-400 kg of OPC in OPC concrete. Three cubic metre of OPC concrete will make use of one ton OPC which is responsible for one ton CO_2 emission, while NaOH usage will only be 36 kg resulting 0.018 ton of the CO_2 emission per 3 m^3 of LCFG concrete. The second part of alkaline solution is the sodium silicate which is the mixture of varying proportion of SiO_2 and Na_2O with general chemical formulation as $Na_2O.xSiO_2$, also known as water glass. It is manufactured through the hydrothermal dissolution of silica sand in sodium hydroxide to produce a sodium silicate solution of 48% solid and a weight ratio of 2 (2 parts SiO_2 to 1 part Na_2O). The energy requirement for the production of this hydrothermal liquor is 500 MJ per ton [4], while cement production requires about 4,400 MJ per ton (International Energy Agency, 2007). For three cubic meter of LCFG concrete sodium silicate solid requirement is in the order of 132kg against one ton of OPC cement with an energy requirement of 66MJ, responsible for 0.015 ton of CO_2 emission.

So total CO_2 emission associated with the alkaline component for 3 $m^3$of LCFG concrete (using one ton fly ash binder) is in the order of 0.033 ton compared to one ton with OPC concrete.

+ Corresponding author. Tel.: +61 8 94565535(A/H); Fax: +61 8 94565535
E-mail address: didar.cheema@ postgrad.curtin.edu.au

Other factors contributing CO_2 emission are generally associated with transport of an alkaline solution, fly ash and its heat curing requirement. According to Dvidovits, CO_2 emission is in the order of 0 .18 tonne per tonne of geopolymer cement resulting from the combustion of carbon fuel [2]. Due to its 80% reduction of CO_2 footprint Low Calcium Fly Ash based Geopolymer (LCFG) concrete is attracting wide spread attention.

2. Experimental Work - LCFG Concrete & Blended LCFG Concrete Mix

2.1. Steam cured LCFG concrete mix

Past research has shown that LCFG concrete with 100% fly ash binder achieved initial strength in the order of 20MPa when allowed to cure ambiently and increasing gradually over time, approximately 40 MPa in 4 weeks and 50MPa in 12 weeks [5]. Main oxides' mix molar ratios of LCFG concrete mix are given in Table 1 below.

Table 1: Mix Oxides' Molar Ratios of LCFG Concrete Mix Proportion

Molar Oxide Ratios	**Na_2O/SiO_2**	**H_2O/Na_2O**	**SiO_2/Al_2O_3**
Oxides' Mix Molar Ratios (This Research Study)	0.1-0.12	10.6-12	3.89
Hardjito & Rangan (2005), Oxides' Mix Molar Ratios' Range	0.098-0.115	10.0 -12.5	3.89*

The typical fly ash source material composition from Collie Power Station, Western Australia determined by X-Ray Fluorescence (XRF) analysis [3] is detailed in Table 2 below, used as a source material.

Table 2: Low Calcium Fly Ash Typical Composition (Collie Power Station, Western Australia)

Oxides	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**MgO**	**P_2O_5**	**SO_3**	**ZrO_2**	**Cr**	**MnO**	**LOI***
Mass %	53.36	26.49	10.86	1.34	0.37	0.80	1.47	0.77	1.43	1.70	-	-	-	1.39

LCFG concrete mixtures, nominated as G40 (40MPa) and G50(50MPa) when steam cured at 60^{o}C for 24 hours and the compressive strength achieved, are summarised in Table 3 below [6], [7].

Table 3: Low Calcium Geopolymer (LCFG) Concrete Mixture Proportions

Materials		**Mass (kg/m^3)**		**Remarks**
		G40	**G50**	
Coarse Aggregates	**14mm**	647	647	
	10mm	647	647	
Fine Sand		554	554	
Fly Ash (Low Calcium ASTM Class F)		409	409	
Sodium Silicate Solution (SiO_2/Na_2O =2)		102	102	
Sodium Hydroxide Solution		41	41	8M & 14M Concentration
Super plasticiser (SP)		6	6	
Water Reducer				Manufacturer specified
Target Water		0	10	
Extra water in aggregates		15.5	24.2	
Admixture				Manufacturer specified
Water/Cement Ratio		0.19	0.20	
Curing Temperature		60 ^{o}C	60 ^{o}C	
Curing Time		24 hours	24 hours	
28 Days Mean Comp (MPa)		54.5	54	

However, due to low initial strength of LCFG concrete with100% fly ash binder when cured ambiently, a blended LCFG concrete with a fly ash (FA) binder containing small proportion of slag was studied, which may be more suitable for in –situ applications as detailed subsequently.

2.2. Blended LCFG concrete ambient & steam cured mix

The typical composition of slag sourced from Cockburn Cement Western Australia used in the blended LCFG concrete mix is summarised in Table 4 below.

Table 4: Typical Slag Composition (Cockburn Cement, Western Australia)

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Fineness	R332	+45um
Ave Mass %	32.4	13	0.65	41.9	5.5	2.2	0.35	0.15	400	72.3	9.2

Oxides' mix molar ratios of blended LCFG concrete with small proportion of slag are summarised in Table 5 below.

Table 5: Mix Molar Ratio of Blended LCFG Concrete

Blended LCFG Concrete	Mix Molar Ratios		
	Na_2O/SiO_2	SiO_2/Al_2O_3	H_2O/Na_2O
5% Slag + 95% FA	0.122	3.927	9.129
10% Slag + 90% FA	0.124	3.961	10.905

An addition of 5% slag to fly ash binder activated by alkaline solution with NaOH solution of 16M concentration raised SiO_2/Al_2O_3 mix molar ratio from 3.89 to 3.93, while 10% slag & additional water raised it to 3.96. Corresponding increase in Na_2O/SiO_2 mix molar ratios was 0.122 & 0.124 respectively from 0.120.

3. Test Results & Observations

For in -situ applications, a concrete of non- structural concrete class (N) of strength up to 40MPa is generally the requirement, such as, rigid concrete road furniture, where curing under ambient conditions is the practical mean of achieving the desired initial strength. Strength achieved by blended LCFG concrete mix with small proportion of slag cured ambiently relative to steam curing are summarised in Table 6 below [6].

Table 6: Blended LCFG Concrete Mixture Proportions

Materials	Mass (kg/m^3)	Mass (kg/m^3)	Remarks
	G40/50	G40/50	
Coarse Aggregates 14mm	647	647	
Coarse Aggregates 10mm	647	647	
Fine Sand	554	554	
Fly Ash 95%(ASTM- Class F)	388.5	388.5	
Slag (5%)	20.5	20.5	
Sodium Silicate Solution (SiO_2/Na_2O =2)	102	102	
Sodium Hydroxide Solution	41	41	16M Concentration
Super plasticiser (SP)	6	6	
Target Water	0	0	
Extra water in aggregates	0	0	
Water/Cement Ratio	0.17	0.17	
Curing Temperature	Steam(60 ^oC)	Ambient	
Curing Time	24hours	De-moulding after 5 days	14 days wet curing
3 Days Mean Comp. Strength(MPa)	55.5		
7 Days Mean Comp. Strength(MPa)		66.5	
28 Days Mean Comp. Strength(MPa)		80.5	

Blended LCFG concrete mix achieved high early strength under ambient curing conditions over a significantly shorter duration and could be a potential construction material for in-situ applications.

The initial dry curing of slag based LCFG concrete under ambient conditions indicated the need of some protection requirement such as polyethylene sheeting to reduce quick loss of moisture for 5 to 7 days. Seven days initial compressive strength gain of slag based LCFG concrete is three times higher than the ambient cured LCFG concrete containing 100% low calcium fly ash activated by 8M alkaline solution [5]. This increased strength gain trend of slag based LCFG concrete was in concurrence with Skvara's study [8].

However slag based LCFG concrete cured at elevated temperature of 60^{o}C for 24 hours resulted slightly lower strength of 55.5MPa. This could be due to the formation of Calcium Silicate Hydrate (CSH) products interfering with polymerisation process [9]. An alkaline activator solution of high concentration (16M-

Sodium Hydroxide) may tend to reduce this initial interference by allowing the polymerisation process to proceed first, which could be due to the fast dissolution, gelation and polymerisation followed by formation of CSH products during the synthesisation of mix constituents. The formation of CSH products in an alkali activated blended LCFG concrete mix have the potential to render discontinuous pore structure with increased tortuosities, while higher strength gain under ambient conditions is also an indirect indication of its durability [6]. Low diffusion coefficient result of alkali activated slag based concrete shown by Sanjayan study [1] is notional that ambient- cured blended LCFG concrete may be more durable than LCFG concrete. Resulting higher strength mix could be attributive to higher mix molar ratios of SiO_2/Al_2O_3 and Na_2O/SiO_2 and may have finer pore structure [8]. Also blended LCFG concrete mix maintained relatively higher pH for specimens exposed to seawater for one year as shown in Table 7 below.

Table 7 Blended LCFG Concrete pH and Compressive Strength and Impact Seawater Exposure

Blended LCFG Concrete	pH		Compressive Strength MPa	
	5% Slag Mix	10% Slag Mix	5% Slag Mix	10%Slag Mix
Steam-24 hours at 60°C	11.1		55.5	
Ambient (Summer)	11.3		66.5	
After One Year Seawater Exposure				
Steam –24 hours at 60°C	10.7	10.9	43	64
Ambient (Summer)	10.6		53	

Fig. 1 below shows the pH trend of blended LCFG concrete before and after seawater exposure of one year relative to the LCFG concrete after severe field exposure.

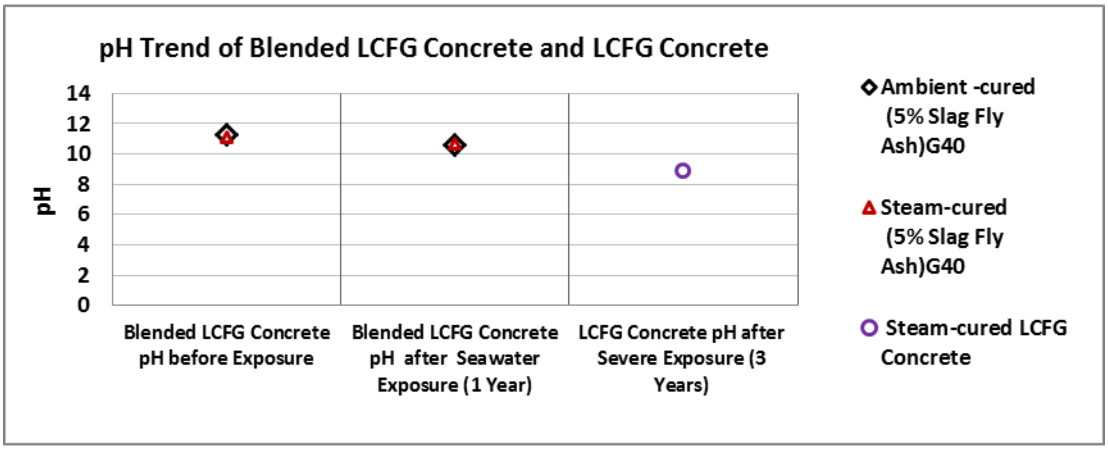

Fig. 1: pH trend of LCFG Concrete & Blended LCFG Concrete Relative to OPC Concrete

Blended LCFG concrete mix with 20% slag resulted early setting, which potentially could be due to high concentration of NaOH (16M) used in the alkaline solution resulting low water/binder ratio for the polymerisation of silicate and aluminate from the source material or quick formation of (CSH) and aluminium-substituted calcium silicate hydrate (CASH) [10] before polymerisation or a combination of these and may need further research.

4. Concluding Remarks

Blended LCFG concrete with slag component less than 20% may be the potential construction material for rigid road and rail furniture structures such as crash barrier, noise wall, traffic island infill, dual use footpath, rest area and kerbing where ambient curing is practical & feasible for the gain of initial required strength and pre-cast components such as rail sleepers, box culverts for underpasses, drainage pipe where steam and ambient curing are feasible. Due to its low pH environments than the conventional Ordinary Portland Cement (OPC) concrete, blended LCFG concrete application scenarios in non-aggressive environments may result considerable saving in CO_2 emission. Both fly ash & slag in blended LCFG concrete being by-products will be of significant benefit environmentally from sustainability & zero waste management perspective and will be of alleviating nature to any downstream health issue which otherwise can occur from heavy metal traces' build- up from fly ash disposal over time, impacting arable soils and ground water.

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