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Zeta potential, gel formation and compressive strength of low calcium fly ash geopolymers

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HIGHLIGHTS

- Workability is a key factor in the properties of low calcium fly ash geopolymer.
- Particle size smaller than 20 μm is best indicator of the suitability of fly ash.
- Specific surface area of fly ash leads dissolution, coagulation and gel formation.
- Negative zeta potential for the fly ash is indicative of a more reactive material.
- A smaller negative zeta potential of geopolymer indicates more gel formation.

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ABSTRACT

A major challenge in the specification of geopolymer mix designs is the variability in the fly ash used and the impact of that variability on the performance of the geopolymer produced. The factors affecting the performance of geopolymers made from a total of five chemically and physically distinct fly ashes are reported. The key factor identified as influencing the strength was the workability, with a flow in the range between 110 ± 5% and 140 ± 5% required for optimal performance. In this flow range, the strength of geopolymer is governed by the specific surface area of precursor fly ash coupled with the quantity of the 10 μm and 20 μm particles. In addition a negative zeta potential of the fly ash was identified as assisting gel formation with the smaller the negative zeta potential of the geopolymer product the more gel formation and high compressive strength observed.

1. Introduction

Portland cement is the most widely used binder in the concrete industry. Its annual worldwide production is expected to grow from approximately 2.54 billion tonnes in 2006 to 4.38 billion tonnes in 2050 based on 5% growth per year [1]. However, the projected level of cement production for 2015 was reached by 2011. Cement production alone contributes between 4% and 8% of the current anthropogenic carbon dioxide (CO_2) emissions worldwide [2–4], with the production of 1 tonne of cement producing from 0.6 up to1 tonne of CO_2, depending on the power plant [5–7]. It is estimated that up to 0.54 tonne of CO_2 per tonne of clinker is released during calcination, in which limestone is transformed into lime, and 0.46 tonne of the CO_2 emitted is the result of burning fuel to provide the thermal energy necessary for calcination to occur [8]. Thus the primary difference between the cement industry and most other industries is that fuel consumption is not the dominant driver of CO_2 emission. Hence, a small reduction of Portland cement production could result in significant environmental benefits in terms of CO_2 emission. This has encouraged research into environmentally friendly cementitious materials producing high strength and good durability while maintaining an acceptable level of energy consumption for production.

It is recognised that alkali additions to fly ash can activate this material to set and harden thereby forming an alkali-activated system, widely known as geopolymer [9–11]. The most emphasized advantage of this is the reduction of CO_2 emission by 26–45% with the replacement of Portland cement with no adverse economic effects [12–14].

Fly ash production had increased to 900 million tonnes per year by 2008 and it is anticipated to increase up to about 2000 million

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tonnes in 2020 [15]. While about 45% of this is being utilized for various purposes including cement and concrete production the balance is disposed in landfills and storage lagoons at significant cost, posing a potential risk to local aquifers due to the possible leaching of heavy metals. Thus, an added benefit is to convert a waste product into a useful by-product, conserving landfills and storage lagoons [16].

Extensive research has been published on the development of fly ash based geopolymer using a wide range of mix designs and activators with distinct variations in compressive strength being noted [11,17–19]. However, to date limited research has been undertaken on understanding the impact of the variations in the chemical composition and physical properties of the precursor fly ash material used and how their interaction determine the strength of the geopolymer produced [20–22]. Activation of the fly ash has been hypothesised as being due to a number of factors, both the Activator Modulus (AM) and the Na_2O dosage have been identified as having a significant impact upon the strength [11,18,23,24]. The AM is defined as the SiO_2 to Na_2O ratio in alkali activator solution and the Na_2O dosage is described as the percentage of Na_2O to fly ash ratio in the alkali activator solution, while previously the activator dosage was considered in terms of the mass ratio of Na^+ to fly ash [25].

The mix design for geopolymer concrete is normally based on the dosage and AM but the fly ash material can have distinctly different properties, including the chemical composition, fineness, the relative content of SiO_2 and Al_2O_3 to each other and the activator, the amorphous content and unburnt carbon, which have all been identified as influencing the strength development [22,26–30].

This paper reports an investigation of the effects of the chemical composition and physical characteristics on the compressive strength of five different fly ash based geopolymers over a range of AM at a fixed Na_2O dosage. The five fly ash materials were all low calcium, class F fly ash, but with varied chemical composition and physical properties, reflecting the range of fly ash materials readily available to make geopolymer concrete. The optimum 28-day compressive strength of each fly ash based geopolymer was determined. In addition the physical properties, the workability and zeta potential have been examined to understand the reasons behind the observed variation in strength.

2. Experimental

2.1. Materials

Fly ash used in the investigation was dry, low calcium class F fly ash conforming to AS 3582.1 standard [31], obtained from five different power plants. The chemical composition and the particle size distribution of the fly ashes, as determined by X-ray fluorescence (XRF) analysis and Malvern Particle size analyser (Mastersizer X) respectively, are summarized in Tables 1 and 2. Brunauer Emmett Teller (BET) method by N_2 absorption was used to determine the specific surface area of fly ash materials.

The alkaline liquid used in geopolymers consisted of a mixture of commercially available sodium silicate solution with a specific gravity of 1.53 and an alkaline modulus ratio (Ms) equal to 2 (where $Ms = SiO_2/Na_2O$, $Na_2O = 14.7\%$ and $SiO_2 = 29.4\%$ by mass), and sodium hydroxide solution (15 M). The sodium hydroxide solution was prepared by dissolving commercial grade sodium hydroxide pellets with 99% purity in deionised water at least one day prior to usage.

Locally available river sand in uncrushed form with a specific gravity of 2.5 and a fineness modulus of 3.0 served as fine aggregate. This was prepared in accordance with AS 1141.5 standard [32]. The demineralized water was used throughout the experiment.

2.2. Mix designs

For all the mortar mixes, the sand to fly ash ratio is fixed to 2.75 according to ASTM C109/C109M standard [33] while the water to solid ratio is fixed to 0.37. The quantity of water contained in the mix is defined as sum of water contained in the sodium silicate, sodium hydroxide and added water, while the quantity of solid is the sum of the mass of fly ash and the solid contained in the alkaline activator solution. Nine mix designs based on AM (Eq. (1)) were used in the investigation.

$$AM = \frac{SiO_2 \text{ in alkaline activator}}{Na_2O \text{ in alkaline activator}} \quad (1)$$

The mix proportion used in each mix design is summarized in Table 3. The AM is varied by blending liquid sodium silicate and sodium hydroxide in different proportions. The Na_2O dosage is kept to 15% by mass of alkali for all mix designs. Previous studies had shown that a Na_2O dosage of 15 produced the highest strength for geopolymer mortar [18]. The mortar specimens investigated, with reference to the fly ash type and mix design, are shown in Table 4.

Table 1
Chemical composition of low calcium fly ash.

Chemical	Component (wt.%) of each fly ash				
	Gladstone (GFA)	Port Augusta (PAFA)	Collie (CFA)	Mount Piper (MPFA)	Tarong (TFA)
SiO_2	50.82	49.97	52.67	65.18	73.12
Al_2O_3	29.89	31.45	29.60	25.30	21.50
$SiO_2 + Al_2O_3$	80.71	81.42	82.27	90.48	94.62
SiO_2/Al_2O_3	1.7	1.6	1.8	2.6	3.4
Fe_2O_3	10.26	3.22	11.27	1.90	1.36
CaO	3.24	5.03	0.94	0.63	0.29
K_2O	0.58	1.87	0.65	3.65	0.63
TiO_2	2.05	2.54	1.83	1.53	1.84
P_2O_5	1.61	1.77	1.13	1.21	1.06
MgO	0.80	1.54	0.72	0.00	0.00
Na_2O	0.00	1.85	0.00	0.00	0.00
SO_3	0.28	0.33	0.48	0.23	0.00
LOI[a]	0.43	0.51	0.63	1.30	1.16

[a] Loss on ignition (unburnt carbon content).

Table 2
Particle size distribution of low calcium fly ash.

X	Passing (%) at X of each fly ash				
	Gladstone (GFA)	Port Augusta (PAFA)	Collie (CFA)	Mount Piper (MPFA)	Tarong (TFA)
5 micron	24.8	30.1	26.1	17.4	22.7
10 micron	43.1	46.7	40.9	36.0	43.0
20 micron	61.9	62.1	54.6	57.1	63.0
30 micron	73.2	71.4	62.7	69.9	73.6
40 micron	79.8	77.4	67.7	77.4	79.3
45 micron	82.7	80.2	70.0	80.7	81.8
50 micron	85.3	82.9	72.3	83.8	84.2
60 micron	89.6	87.9	76.7	89.0	88.3
70 micron	91.2	90.1	79.0	91.2	90.2
80 micron	92.6	92.1	81.3	93.0	91.9
90 micron	93.8	93.8	83.6	94.6	93.4
SSA[a]	2362.7	1228.3	1095.3	1025.5	1875.5

[a] Specific surface area (m^2/kg).

2.3. Specimen preparation and curing

The fly ash and sand were mixed using a 5-l Hobart mixer for 4 min. Activator solution and water was added to the dry mix and mixed by hand for 1 min. The whole mix was then blended in a Hobart mixer for 4 min with a speed of 150 rev/min and further 2 min with 300 rev/min. Immediately after mixing the geopolymer mortar was placed in $50 \times 50 \times 50\ mm^3$ Teflon moulds and vibrated using a vibration table for 20 s. After vibration the moulds were kept at room temperature for 1 day and then cured in an oven for 24 h at 80 °C temperature with 95% relative humidity. Moulds were removed from the oven and left to cool to room temperature before demoulding, and then kept at room temperature until being tested.

2.4. Test procedure

The compressive strength test was performed on the $50\ mm^3$ specimens in accordance with AS 1012.9 standard [34] and a loading rate of $0.34\ N/mm^2/S$ using a Technotest concrete testing machine. The reported 28-day compressive strength