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Performance of solid and cellular structured fly ash geopolymers exposed to a simulated fire

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ABSTRACT

This paper reports on the effects of simulated fire exposure on solid and low density, cellular structured geopolymers in order to assess their suitability for high temperature applications such as thermal barriers and fire resistant panels. Geopolymer mixes with designed Si:Al ratios of 2.5 were synthesised from three different class F fly ashes. Low density samples were produced by adding a small amount of metallic aluminium to the geopolymer slurry which reacted with the free NaOH to produce a cellular structure in the hardened material. Physical properties of the materials are presented as well as results from scale fire tests. An international standard fire curve (ISO 834) was used to simulate the heating conditions of a fire. Fire testing was conducted on 50 mm thick panels with an exposure region of 200 mm × 200 mm. Fire ratings of more than 90 min were achieved with water content and resistance to shrinkage cracking identified as important sample parameters.

1. Introduction

Geopolymers are a broad class of material produced by the dissolution and polycondensation of aluminosilicates in highly alkaline solutions. This class of material is also commonly referred to in the literature as 'inorganic polymers' or 'alkali activated cements'. They can be produced from a wide range of source materials which in turn gives them a wide range of physical properties. This allows geopolymers to exhibit properties that can make them suitable for applications ranging from conventional binders to high temperature resistant insulators.

One of the promising source materials for the synthesis of geopolymers is fly ash. Fly ash is a by-product from coal fired power stations and has been shown to be highly suitable for producing geopolymers, including the production of thermally resistant geopolymers [1,2]. It has been reported that the spherical shape of the fly ash particles allows for better workability at low water contents than other source materials, meaning that samples can be synthesised with less water which in turn reduces dehydration shrinkage upon high temperature exposure [1].

A number of researchers have investigated the thermal properties of fly ash geopolymers exposed to uniform heating regimes in a furnace [1–4]. The impressive thermal properties of geopolymers suggest they could also be suitable for use in fireproofing applications where the material would have to be capable of withstanding non uniform heating at much greater heat rates. This paper presents the results from an investigation of fly ash geopolymers exposed to fire-like heating regimes.

A number of standards have been developed to test and compare the performance of fire proofing materials during a fire. The international standard ISO 834 [5] contains the most commonly adopted fire curve and is based on a cellulose fire (as opposed to a hydrocarbon fire), and is also adopted by the Australian standard AS1530.4 [6], Norwegian standard NT Fire 046 [7] standards and Eurocode EN1991-1-2 [8]. The time versus temperature relationship of this fire curve is described in the following equation :

$$T = 345\log_{10}(8t + 1) + 20 \quad (1)$$

where T is the temperature (°C), t is time (min).

Lowering the density of solid materials is known to reduce their thermal conductivity and hence increase their ability to insulate [9]. As such, the scope of this research was expanded to include the analysis of low density, cellular structured geopolymers along with solid samples. Geopolymers can by synthesised with a cellular structure by inducing chemical reactions that either entrain air or release gasses to foam the structure prior to the gel hardening [10,11]. The degree of foaming can be controlled by varying the concentration of the foaming agent. Typically, foamed geopolymers exhibit densities ranging between 0.4 and 1.2 g/cm^3. As geopolymer density reduces, the mechanical properties are also known to reduce [12], though the ability of the sample to insulate has generally been found to improve [9,13]. Fibre reinforcement in cellular structured geopolymers has been shown previously to aid in the synthesis of a uniformly foamed material by reducing pore collapse prior to hardening [9] and also to improve the resistance

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to dehydration damage during high temperature exposure by increasing the permeability [14]. Fibres with a low melting point, such a polypropylene (160–175 °C) [15], are most effective as they create dehydration pathways (gaps in the structure where fibres were prior to decomposition that promote the passage of water vapour) at relatively low temperatures [16].

This paper reports on the physical properties and fire resistance of solid and cellular structured fly ash geopolymers synthesised from three different ashes. Aluminium powder and polypropylene fibres at fixed concentrations were added to make cellular structured mixes from the solid mix formulations.

2. Experimental

2.1. Materials

Three class F fly ashes from Eraring, Tarong and Port Augusta power stations in Australia were used in this study. Full details of the quantification of these fly ashes can be found in Rickard et al. [3,17], though a summary is provided in Table 1.

Activating solutions (sodium silicate/aluminate) were selected to either raise or lower the Si:Al ratio of the geopolymer made from the different fly ashes in order to achieve a common ratio between the samples. Sodium silicate solutions, used for the Port Augusta fly ash geopolymers, were prepared by dissolving sodium hydroxide pellets (Univar Pty. Ltd.) and deionised water into PQ-D (29.4 wt.% SiO_2, 14.7 wt.% NaOH, 55.9 wt.% H_2O) from PQ Corporation. Sodium aluminate solutions, used for the Eraring and Tarong geopolymers, were supplied by Coogee Chemicals who specified that the solution contained 19 wt.% Al_2O_3, 25.5 wt.% NaOH and 55.5 wt.% H_2O. Aluminium powder with a particle size of 50 μm and a purity of 99.5% (product code AL006020, Goodfellow, UK) was used for foaming. 100% virgin monofilament polypropylene fibres (Sika Australia Pty. Ltd.) with specified dimensions of 18 mm (length) and 22 μm (diameter) were used to stabilise the foamed samples.

2.2. Geopolymer synthesis

Geopolymers were synthesised with compositional ratios of Si:Al = 2.5, Na:Al = 1.25 and a water content of between 18 and 22 wt.%, adjusted for workability. Samples were made by mixing the fly ash and activating solution in a Hobart mixer (Hobart Corp., USA.) for 5 min. The cellular structured variants of the mixes additionally had fibres, at a concentration of 0.25 wt.%, gradually added to the slurry with the mixer on a low speed to achieve a uniform dispersion. Aluminium powder was added at a concentration of 0.05 wt.% to form the cellular structure and the slurry was mixed for a further 30 s. Immediately after mixing the slurry, samples were poured into various sized moulds, sealed and left to cure in an oven at 70 °C for 24 h. The moulds for the foamed samples were only half filled to allow the slurry to expand unrestricted as the aluminium powder reacted.

Table 1
Composition of each of the fly ashes. Values in parentheses are the standard deviation of the least significant figure displayed to the left in the table.

	Port Augusta (wt.%)	Eraring (wt.%)	Tarong (wt.%)
Amorphous			
SiO_2	24.53 (67)	45.03 (65)	42.79 (59)
Al_2O_3	11.14 (45)	7.67 (32)	4.11 (26)
Fe_2O_3	1.03 (17)	2.49 (16)	0.64 (2)
CaO	4.60 (5)	1.59 (5)	0.08 (5)
Other	8.93 (25)	5.64 (25)	3.15 (25)
Crystalline			
Quartz	19.99 (75)	14.89 (30)	24.08 (27)
Mullite	26.83 (33)	20.88 (14)	25.10 (11)
Hematite	0.87 (38)		
Magnetite		1.49 (52)	
Maghemite-C	0.85 (27)		
Rutile	0.74 (50)		
Amorphous Si/Al (molar)	1.87 (6)	4.98 (19)	8.84 (49)

2.3. Mechanical testing

Compressive strength testing was conducted on cylinders with a 50 mm diameter and 100 mm height using a Lloyds universal tester EZ50 (UK). A load rate of 0.25 MPa/s was used to closely comply with ASTM C39 [18]. Samples were tested 28 days after synthesis and the stated strength values are the average of the results from at least 3 samples.

2.4. Density

The density of the samples was determined by dividing the mass by the volume. Cylindrical samples (50 mm diameter, 100 mm high) were used for density measurements. All reported density results are the average of measurements from 5 samples.

2.5. Thermal conductivity

Thermal conductivity was measured using the embedded hot wire method. A 0.32 mm diameter nickel–chromium heating wire was embedded during casting in a cylindrical sample of dimensions 100 mm (diameter) × 160 mm (height). The samples were heated by applying a 2 V, 1 A current through the heating wire and the sample temperature was logged by an embedded type K thermocouple. The temperature was logged for 10 min and the thermal conductivity (k) was calculated using Eq. (2). Full derivation of the equation can be found in [19].

$$k = \frac{VI}{4\pi La} \tag{2}$$

where V is the voltage (V), I is current (A), L is length of heating strip (m) and a is gradient of temperature rise versus the natural log of the time in seconds.

2.6. SEM

Scanning electron microscopy (SEM) was conducted on a NEON 40EsB (Zeiss, Germany) with a field emission source. Sample fragments were mounted onto aluminium stubs and out-gassed in a desiccator over a 48 h period before being coated with a 4 nm layer of platinum prior to imaging in the SEM.

2.7. Fire testing

Fire testing was conducted to closely comply with Australian standard AS1530.4 [6]. A custom designed electric furnace was used for the fire testing (Fig. 1). 290 × 290 mm panels with a thickness of 50 mm were synthesised for the fire testing. The sample exposure region was 200 × 200 mm. The furnace temperature was controlled using a multi stage controller (model PAK-700, Furnace Technologies Pty. Ltd.) programmed to follow the time–temperature relationship in Eq. (1). Three type K thermocouples were placed on the cold side of the sample. Cold side temperatures were recorded individually and as the average of the three thermocouples. The data for the thermocouples was logged every 3 s using a Vernier LabQuest (USA).