Construction and Building Materials 24 (2010) 1906–1910

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Preparation and characterisation of fly ash based geopolymer mortars

J. Temuujin [a,*], A. van Riessen [a], K.J.D. MacKenzie [b]

[a] Centre for Materials Research, Department of Imaging and Applied Physics, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia
[b] School of Chemical and Physical Sciences, Victoria University of Wellington, New Zealand

ARTICLE INFO

Article history:
Received 16 December 2009
Received in revised form 12 March 2010
Accepted 1 April 2010
Available online 20 April 2010

Keywords:
Geopolymer
Fly ash
Mortar
Compressive strength
Bonding

ABSTRACT

Geopolymer mortars with varying levels of sand aggregate were prepared and their physical and mechanical properties studied. The geopolymer binder to sand aggregate weight ratio was varied from 9 to 1. Compressive strength and Young's modulus of the fly ash based geopolymer paste were 60 MPa and 2.27 GPa and these values did not change significantly with addition of up to 50 wt.% sand aggregate. Geopolymer binder exhibited strong bonding to the sand aggregate. Increasing sand content without increasing the amount of alkaline activator resulted in a decreasing level of geopolymerisation within the binder system.

1. Introduction

In the last decade fly ash based geopolymer has emerged as a promising new cement alternative in the field of building and construction materials [1–3]. Geopolymers exhibit many excellent properties such as high compressive strength, low creep, good acid resistance and low shrinkage [3]. Geopolymers described in this paper were manufactured from fly ash which is a solid residue arising from coal burning thermal power stations and is thus very beneficial in terms of environmental impacts. Hardjito and Rangan [3] demonstrated that one tonne of low-calcium fly ash can be used to produce 2.5 m^3 of high quality geopolymer concrete that is cheaper than Portland cement concrete. Fly ash geopolymers have been prepared as geopolymer pastes [4], mortars [5] and concretes [2,3]. For the production of mortar and concrete, natural or industrially manufactured aggregate is added as filler as it is less expensive than the paste. The inclusion of naturally occurring materials such as quartz, basalt, granite, sandstone and limestone as aggregates to geopolymer paste is not only economically favourable but also reduces pore density, reduces crack formation and improves durability [6]. In ordinary Portland cement (OPC) concrete and mortar there is a likelihood of an alkali-aggregate reaction between reactive aggregate and alkalis present in cement ($Na_2O + K_2O$) and $Ca(OH)_2$. The product of the alkali-aggregate reaction results in expansion and subsequent crumbling of the mortar and concretes. Garcia-Lodeiro et al. found that the calcium in the OPC mortar plays an essential role in the expansive nature of the gels [7]. Fly ash based geopolymer mortars are less susceptible to alkali-aggregate reaction because the lower calcium content in these systems results in a reaction product that is not expansive [7,8].

Previous researchers have described addition of aggregate to geopolymer with binder: aggregate at constant ratio 0.5 [5]. Determination of the optimal binder: aggregate ratio is important for resource efficiency and meeting specified mechanical properties of mortars. The present research reports on the effects of aggregate content on the geopolymerisation process within the binder phase and subsequent mechanical properties of the mortar.

2. Experimental

2.1. Preparation

Geopolymer was manufactured from Collie fly ash from Western Australia. The fly ash consists of wt.%: 60(1) amorphous composition, 20(1) quartz low, 17(1) mullite, 1.7(0.5) maghemite (Q) and 0.9(0.5) hematite [4]. The values in brackets indicate the uncertainty. The median size d_{50} of the fly ash was 14.4 μm. The aggregate used was bricklayer's sand purchased from a local hardware store. The granulometry distribution of the sand (aggregate) is shown in Fig. 1. The granulometry distribution was obtained by shaking the sand through a sieve set with sizes of 1180, 750, 600, 425, 250, 150 and 75 μm, respectively. The grading curve of the sand aggregate indicates that the fineness of the sand is lower than that specified as the low limit for fine aggregates for concrete according to ASTM C33.

Characteristics such as fineness modulus and apparent dry density of the aggregate are important factors for determining mortar properties which is usually determined by utilising a standard sieving method with exact mesh sizes [9]. The sieves used for the granulometric distribution of the aggregate were not the same as required for determination of the fineness modulus and therefore, the fineness modulus was not calculated. The apparent dry density or bulk density of the aggregate was calculated by dividing the mass of non-compacted dry aggregate (dried at

* Corresponding author. Tel.: +61 8 9266 3673.
E-mail address: jtemuujin@yahoo.com (J. Temuujin).

0950-0618/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.conbuildmat.2010.04.012

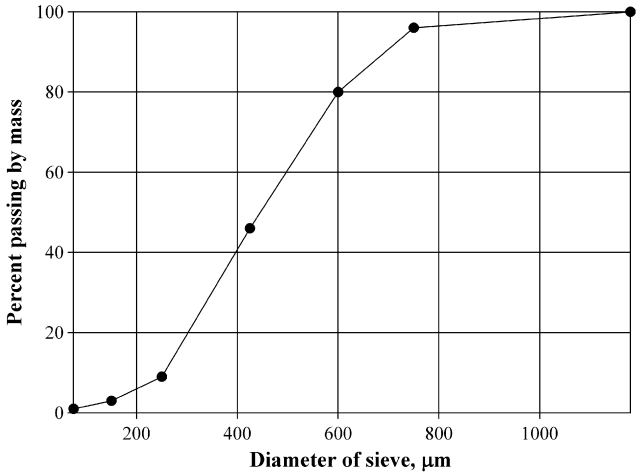

Fig. 1. Grading curve of sand aggregate.

105 °C) to the volume of a 100 ml glass cylinder containing the dried aggregate. The apparent dry density of the sand was 1416(10) kg/m^3. The value in the bracket is the standard deviation of three separate measurements.

An XRD pattern (not shown here) of the sand revealed the presence of quartz with a minor amount of microcline. The chemical composition of the fly ash and aggregate as determined by X-ray fluorescence are presented in Table 1.

The binder composition of the geopolymer mortar was calculated based on the amorphous composition of the fly ash assuming the amorphous alumina and silica of the fly ash are the reactive components. The method used to determine the amorphous composition of Collie fly ash is described elsewhere [10]. The content of the amorphous Al_2O_3 and SiO_2 in fly ash were 11.64 wt.% and 26.49 wt.%, respectively. For geopolymer described in this paper a formulation determined by Hardjito and Rangan was used for the same Collie fly ash [3]. However, we have re-calculated the geopolymer formulation using the only the amorphous composition of the fly ash and obtained Si:Al = 2.3 and Na:Al = 0.88 [4]. Since we used only the amorphous part of the fly ash to determine the geopolymer formulation less alkaline activator is used than that used by the previous authors [3]. The activating solutions used were sodium silicate D-51 from PQ Australia Pty., Ltd. with a chemical composition of (wt.%): Na_2O = 14.7, SiO_2 = 29.4 and water = 55.9 and 14 M sodium hydroxide solution prepared from analytical grade sodium hydroxide pellets.

The compositions of the geopolymer mortars are shown in Table 2.

As mentioned above the fly ash consists of an amorphous part (~60 wt.%) and a crystalline part (~40 wt.%). The crystalline part of the fly ash has low reactivity and can be considered as fine aggregate. Therefore the geopolymer mortar contains geopolymeric (aluminosilicate) gel, crystalline fine aggregate present in fly ash and added sand aggregate. The weighed components for the paste were mixed in a centrifuge mixer (Thinky Co., Japan) at 1300 rpm for 5 min. followed by de-foaming at 2100 rpm for 30 s. The paste was then placed in cylindrical plastic moulds with 25 mm diameter and 50 mm height. The capped moulds were cured at 70 °C for 24 h. After curing the moulds were removed from the oven and kept at ambient temperature for 3 days followed by de-moulding. For compressive strength testing the samples were cut flat with a diamond saw. Mortars were prepared the same way, however, it was noted that for the 40 and 50 wt.% aggregate samples workability was low.

2.2. Test methods

The XRD patterns of the fly ash and sand (aggregate) were collected on a Bruker D8 Advance Diffractometer using Cu Kα radiation. Diffraction patterns were collected from 10° to 80° 2θ. The step size was 0.02° 2θ with a scan rate of 0.6° 2θ/min. Geopolymer-aggregate interfaces in the mortars were studied with a Zeiss EVO 40XVP scanning electron microscope on a fracture surface. SEM micrographs were taken within 2 weeks of sample preparation. Aggregate distribution at macroscopic level was observed with a Nikon SMZ 800 light microscope using sectioned geopolymer mortar samples. The ^{27}Al MAS NMR spectra of the samples were acquired at 11.7 T using a Varian Unity 500 MHz spectrometer and 5 mm Doty MAS probe in which the sample was spun at 10–12 kHz and a 15° pulse of 1 μs and recycle time of 1 s were used and referenced to $Al(H_2O)_6^{3+}$. Seven days compressive strength tested samples were immediately ground and used for NMR analysis. NMR spectra were taken approximately 1 month after preparation of the geopolymer mortar.

Table 2
Compositions of the geopolymer mortars.

	Fly ash, wt.%	Sodium silicate, PQ, D-51, wt.%	Sodium hydroxide (14 M), wt.%	Sand, wt.%	Binder:sand, wt. ratio
Paste	73.91	18.63	7.45	–	–
Mortar – 10%	66.52	16.77	6.70	10	9.0
Mortar – 20%	59.12	14.89	5.95	20	4.0
Mortar – 30%	51.74	13.04	5.21	30	2.3
Mortar – 40%	44.33	11.17	4.47	40	1.5
Mortar – 50%	36.96	9.31	3.72	50	1.0

Seven day compressive strengths of the samples were measured with an EZ-50 Universal testing machine (Lloyd Instruments). ASTM C39 for determination of compressive strength of cylindrical concrete specimens was used as a guide. We followed the standard by using a 2:1 aspect ratio for cylindrical samples (length:diameter) and applying a load rate 0.25 MPa/s. The standard was not strictly adhered to because it was used for mortar rather than concrete and using an instrument without a bearing stage. The compressive strength and Young's modulus values are thus treated as relative measures enabling us to compare different samples. The uncertainty in the measurements was taken as the standard deviation of the compressive strength of four samples. The Young's modulus of each sample was calculated from the linear stress/strain response by Lloyd Instruments *Nexygen Plus* material test data analysis software.

Changes of open porosity and density were measured by Archimedes principle using the sectioned samples with height of about 5–7 mm. For each composition the average of two specimens were used to obtain density and open porosity values. Values in brackets indicate the standard deviation. The measurements were performed 8 days after sample preparation. Since, de-ionized water was used as the liquid medium, the porosity and density should be considered as relative values because of possible leaching of Na ions into the water.

3. Results and discussion

Geopolymer mortars with 10–30 wt.% of aggregate exhibited acceptable flowability while the 40 and 50 wt.% aggregate containing mortars were stiff and difficult to pack into the plastic moulds. An optical micrograph of the 50 wt.% aggregate containing mortar (Fig. 2) revealed that the aggregate was distributed homogeneously within the geopolymer binder. Sectioning of the mortar by diamond saw did not cause any interfacial cracks between sand and geopolymer binder at a macro level.

The compressive strength of the mortar remains essentially constant with varying aggregate content (Fig. 3). Differences between the mean values of different mortar samples are not significant when taking into account uncertainties of two standard deviations (2σ). The compressive strength of the geopolymer mortar depends on the strength of the geopolymeric gel, the interfacial bonding between the geopolymeric gel and aggregate and to some extent the aggregate itself. The results suggest that the interfacial bonding between aggregate and geopolymer was comparable in strength to the geopolymer and/or the sand aggregate by themselves.

Physical and mechanical properties of the geopolymer mortars are summarized in Table 3.

As the level of aggregate was increased the open porosity decreased. There is a decrease in open porosity from paste to mortar with 50 wt.% aggregate of 37.8% that is accompanied by an increase in density of 14.5%. The density of a geopolymer gel is reported to

Table 1
Chemical composition of fly ash and aggregate, wt.%.

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	SO_3	TiO_2	LOI
Aggregate	3.59	0.02	1.29	1.08	–	–	0.13	–	87.05	–	–	–
Fly ash	23.63	1.74	15.3	0.84	1.2	0.13	0.38	1.31	51.5	0.28	1.32	1.78