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Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing

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Abstract

This article reports a study of thermal stability of properties upon firing at 800–1200 °C of geopolymer materials prepared using class F fly ash and Na and K alkaline activators. Compressive strength and shrinkage measurements, XRD, SEM (BEI), TGA and MIP were utilised in these studies. The materials were prepared at water/binder ratios in a range of 0.09–0.35, using compaction pressures up to 10 MPa and curing temperatures 80 and 100 °C. Thermal stability of the studied geopolymer materials was rather low. In the samples prepared using sodium-containing activators rapid deterioration of strength at 800 °C was observed, which was connected to a dramatic increase of the average pore size. Initially amorphous structures were replaced by the crystalline Na-feldspars. In materials prepared using fly ash and potassium silicate compressive strength was significantly increased on heating, deterioration of strength started at 1000 °C. After firing these materials remained amorphous with reduced average pore size and significantly increased compressive strength. Compaction at 1–10 MPa reduced shrinkage on firing in all materials. Geopolymer materials prepared using class F fly ash and alkaline activators showed high shrinkage as well as large changes in compressive strength with increasing fired temperature in the range of 800–1200 °C. Thus the materials were found unsuitable for refractory insulation applications.

Keywords: Fly ash; Alkali activated cement; Thermal resistance; Mercury porosimetry; Microstructure; Compressive strength

1. Introduction

Recently discovered geopolymers are ceramic materials that are produced by alkali activation of aluminosilicate raw materials, which are transformed into reaction product by polymerisation in a high pH environment and hydrothermal conditions at relatively low temperatures (up to 120 °C). Because of the low energy requirements of production from common raw materials and their inflammability at high temperatures, these compounds are attracting increasing interest as ecologically friendly fireproof building materials, sound and heat insulators and materials for encapsulating hazardous wastes for storage or disposal [1,2].

Previous investigations by Davidovits et al [3,4], Barbosa and MacKenzie [5,6] reported very good heat resistant properties of materials prepared using sodium silicate, potassium silicate and metakaolin, having thermal stability up to 1200–1400 °C. Geopolymers can be prepared using fly ash and metakaolin as raw materials. Fly ash is a waste of energy manufacture and is produced in millions of tonnes in every developed country, only 20% of it is utilised. If compared with metakaolin it has low cost and environmental factor of utilisation of waste material polluting the environment. However, it may contain significant amount of impurities like iron oxide in a form of hematite and magnetite, and it is also less reactive than metakaolin. Previous work by Krivenko and Kovalchuk [7] investigated heat resistant geopolymer materials manufactured using class F fly ash, which had good thermal resistance properties up to 800 °C. The aims of this study was to investigate thermal stability up to 1200 °C of geopolymer materials prepared using local fly ashes and compare their thermal behaviour to that of geopolymers prepared using metakaolin.

Geopolymers prepared using either fly ash or metakaolin have framework structures originating from condensation of tetrahedral aluminosilicate units of varying Al/Si ratio such as $(Al–O–Si–O–)M^+$, $(Al–O–Si–O–Si–O–)M^+$, $(Si–O–Al–O–Si–O–Si–O–)M^+$ etc. M^+ is an alkali ion, typically Na or K, which balances the charge of the tetrahedral Al [1]. Geopolymers prepared using class F fly ash are largely amorphous, but depending on the activator used in its preparation, may contain areas of semi-crystalline zeolites such as sodalite, gismondine, and chabazite [8]. This paper investigates the effect

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Table 1
Composition of fly ash (mass %) by XRF

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	Loss on ignition
Fly ash 1[1]	50.0	28.0	12.0	6.5	1.3	0.7	0.2	–	–	–
Fly ash 2[2]	61.4	33.0	1.1	0.6	0.3	0.1	0.1	2.0	–	1.4

1—Gladstone, Queensland, Australia.
2—Tarong, Victoria, Australia.

of the composition and processing conditions on strength and heat resistant properties at temperatures 800–1200 °C of geopolymer materials prepared using class F fly ashes.

2. Experimental

2.1. Materials

The chemical and mineral compositions of two fly ashes used in the investigation are shown in Table 1 and Fig. 1, respectively. Fly ash 1 was sourced from Gladstone in Queensland; Australia. It is mainly glassy with some crystalline inclusions of mullite, hematite and quartz, with particles size range of 1–7 μm. Fly ash 2 was sourced from Tarong power station in Australia. It is glassy with considerable crystalline inclusions of quartz and mullite with particles size range of 1–10 μm. Fly ash 1 contained 50% silicon oxide and 13% iron oxide, while Fly ash 2 contained 61% silicon oxide and 1% iron oxide. Sodium hydroxide and potassium hydroxide (Sigma), sodium silicate type D with M_s (ratio of silica oxide to sodium oxide) equal to 2.02, 14.7% Na_2O, 29.4% SiO_2, and potassium silicate 13.5% K_2O, 27% SiO_2 both supplied by PQ Australia were used in materials preparations.

2.2. Specimen preparation and test conditions

2.2.1. Preparation of specimens

Two series of test samples were made, differing in their composition and method of moulding. Table 2 shows the details of the samples and moulding conditions. In Series1 samples were prepared using sodium hydroxide, potassium silicate and sodium silicate solutions, providing 8–9%Na or K in mixtures and water/binder ratios of 0.27–0.345. Water/binder ratio given in this paper was calculated as a ratio of total mass of water to mass of fly ash. The pastes were cast in plastic cylinders and sealed with the lid. Because of low flow ability of mixes hand compaction using cylindrical plunger was utilised at a filling stage. The compaction was used to eliminate visible voids in the moulding material. In Series 2 Fly ash samples were prepared, providing 8–9%Na or K in mixtures and water/binder ratios of 0.09–0.166. In series 2 mixes of very dry consistency were used, thus some of test samples were pressure compacted. The compaction pressure varied from 1 to 10 MPa (Table 2). The pastes were moulded in plastic cylinders and sealed with the lid. The method of heat curing was developed before in Ref. [8]. It was shown that prolonged initial curing of samples at room temperature before the application of heat was beneficial for strength development of geopolymer samples prepared using fly ash. The method of curing of mixtures of series 1 and 2 was the same, initially samples were cured for 24 h at room temperature, after that the mixtures were ramped either to 80 or 100 °C for series cured, respectively, at 80 and 100 °C, and cured at this temperature for 24 h. After heat curing the oven was turned off and the materials cooled down inside the oven, afterwards the materials were held at room temperature before being used in tests.

2.2.2. Testing conditions

Table 3 shows the summary of experimental programme. The $\phi 25 \times 50$ mm cylinder samples were exposed to firing at 800, 1000 and 1200 °C for 4 h at a heating rate 10 °C/min. The compressive strength of $\phi 25 \times 50$ mm cylinder samples was measured before and after firing. At least three samples were used for each data point in these tests. Before and after firing tests dimensions of the cylinder samples were measured using Vernier callipers. Using these measurements shrinkage of the materials

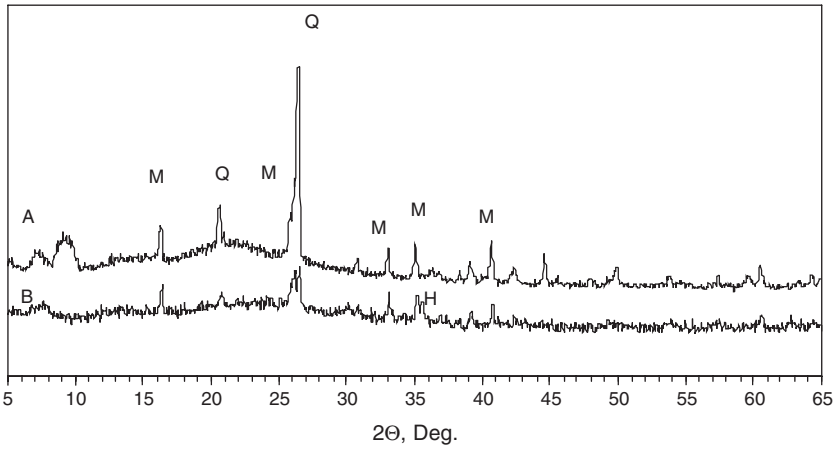

Fig. 1. XRD traces of fly ashes: A=Tarong fly ash, B=Gladstone fly ash; Q=quartz, M=mullite, H=hematite.