

# Strategies to control the high temperature shrinkage of fly ash based geopolymers



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## ABSTRACT

Strategies to control thermally induced shrinkage in fly ash based geopolymers are investigated. The use of low (<2) Si:Al ratios in the geopolymer provides superior thermal properties and the addition of fillers delivered additional improvements resulting in impressive thermal resistance. Two thermally stable inorganic fillers,  $\alpha$ -alumina and wollastonite, were used because of their high melting points and relatively low thermal expansion. Shrinkage events at elevated temperatures revealed that samples containing filler exhibited 30–35% less volume shrinkage than the control at 1000 °C. Initial compressive strength was moderate (~30 MPa), but increased markedly when samples were fired in excess of 600 °C (>100 MPa). Wollastonite addition also improved the flexural strength of the samples which was attributed to its acicular shape imparting fibre-like qualities. Microstructural investigations showed that unfired samples predominantly consisted of spherical particles coated with reaction product. Firing to 1000 °C converted the morphology to a more compact phase with increased pore size.

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## 1. Introduction

Geopolymers are inorganic condensation polymers based on aluminate and silicate entities. Typical sources of aluminosilicates are metakaolin and coal fly ash which are activated by alkaline media releasing the aluminate and silicate oligomers which then condense to form the geopolymer. The resulting structures were initially elucidated by Davidovits [1] as being sialates, sialate-siloxo, and sialate-disiloxo. They are based on silicon and aluminium centred tetrahedra with alkali metal ions providing charge balancing for the  $Al^{3+}$  centres [2].

Geopolymers are a class of binding material with wide applicability from concrete to low density foams [3,4]. Their inorganic nature suggests utility in thermal applications including fire resistant products [4–6]. The range of thermal applications brings different thermal load demands to the geopolymer products. Refractory insulating products are generally exposed to gradual heating rates and long periods at temperature, whilst fire resistant products are designed to be exposed to fast initial temperature increases for a relatively short duration. The cooling cycle after a fire may be rapid due to large quantities of water used to fight the fire or a slower decrease if the fire is allowed to die out due to fuel depletion. Rapid temperature changes can give rise to the formation of cracking due to stresses caused by differences in thermal expansion/contraction. These events are governed by the intrinsic

thermal properties, the values of which also vary with temperature. The physical dimensions of exposed components and the nature of the thermal exposure which can range from one surface exposed to a heat source to totally immersed uniform heat exposure, also play roles in the outcomes of thermal exposure events.

The increased pore volume connectivity of geopolymers compared to OPC will markedly increase transport of water through the binder with associated reduced spalling during high temperature exposure [7,8]. This, together with inherent heat resistance, indicates that fly ash based geopolymers will exhibit improved fire resistance compared to OPC.

Previous work on the thermal properties [9–11] had considered geopolymers produced from fly ashes with target amorphous silicon to aluminium ratios of greater than two. The fly ash amorphous content silicon to aluminium ratio governed the response to thermal exposure with higher ratios giving improved response to thermal exposure up to 1000 °C. The use of low Si:Al ratio to synthesis geopolymers for improved thermal resistance is evaluated. The fly ash used in this work had an amorphous Si:Al ratio of 1.62 and when activated with small amounts of sodium silicate solutions produced a nominal geopolymer Si:Al ratio of 1.82.

Rickard et al. [9] synthesised geopolymers from five different fly ashes at targeted silicon to aluminium ratios of 2.0, 2.5 and 3.0. It was found that reducing the amount of silicate or aluminate added via the activating solutions gave strength gains or strength retention after thermal exposure. Geopolymer made from low silicon to aluminium amorphous ratio fly ash showed good initial compressive strength, which declined rapidly after thermal exposure. Dilatometry of geopolymers produced from this fly ash

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showed large expansive events which were attributed to the expansion caused by the unreacted/residual silicate based material.

In order to optimise thermal properties, control of thermal expansion and retention/development of physical properties during elevated temperature exposure is desirable. The use of thermally stable (filler) materials to minimise thermal expansion/shrinkage is common place in other materials technology. For example the addition of inorganic fillers is known to modify the thermal expansion properties of organic polymers [12,13]. The addition of 40 wt.% wollastonite to polypropylene has been reported to reduce moulding shrinkage from 2.1% to 0.6% leading to improved dimensional stability [13].

Several researchers have evaluated the effect of the addition of aggregates and fillers on geopolymer thermal properties. Subaer and van Riessen [14] investigated the addition of  $\alpha$ -quartz and granite aggregates to metakaolin based geopolymer mortars. Adding 20 wt.% aggregate to the geopolymer reduced the shrinkage by 50% in the range of 23–500 °C. A further reduction in shrinkage was obtained by increasing the aggregate content to 40 wt.%.

Bell et al. [15] evaluated fillers, including 0.8  $\mu\text{m}$   $\alpha$ -alumina in a potassium metakaolin based geopolymer. The fillers were not observed in the microstructure and this was attributed to either the filler particles reacting in the geopolymerisation synthesis or becoming indistinguishable due to a coating of geopolymer gel. The aim of the work was to produce durable materials with outstanding thermal shock resistance suitable for moulds for casting speciality steels at 1428 °C. The alumina filled geopolymer cooled less rapidly than other evaluated systems.

Lin et al. [16] added up to 30 wt.% of 0.75  $\mu\text{m}$   $\alpha$ -alumina to metakaolin geopolymers which had been synthesised by reaction with potassium silicate. Lin also measured the thermal volume shrinkage of specimens after exposure to elevated temperature and observed significant reductions in shrinkage values above 20 wt.% alumina additions. This was particularly marked above 800 °C. From this Lin concluded that the presence of alumina was beneficial for reducing thermal shrinkage. Lin also concluded that the presence of alumina increases the crystallisation onset temperature and also the degree of crystallisation.

Kamesu et al. [17] made potassium activated metakaolin geopolymers which were filled with fine quartz (100  $\mu\text{m}$ –1 mm) or  $\alpha$ -alumina (0.1–100  $\mu\text{m}$ ) to evaluate the thermal properties of the blends. The maximum shrinkage of the control geopolymer was 17% at 1000 °C which was reduced to 12% by the addition of the alumina and to 13% by the addition of quartz. The temperature of maximum densification was shifted from 1000 °C for the control to 1150 and 1200 °C, respectively by the addition of 75 wt.%  $\alpha$ -quartz and alumina.

Silva et al. [18] used naturally occurring wollastonite fibres (aspect ratio = 10 to 20:1) to reinforce a metakaolin based geopolymer. Toughness of the composite increased as fibre volume increased to 5 vol.%. The wollastonite was found to be compatible with the high pH levels utilised in geopolymer paste synthesis and a dense interfacial transition zone, was developed.

In the work presented in this paper fly ash based geopolymers were synthesised with target silicon to aluminium ratios below 2.0 to ensure retention of strength after high temperature exposure. In addition thermally stable fillers ( $\alpha$ -alumina and wollastonite) were incorporated into the geopolymer matrix to improve the thermal resistance by minimising shrinkage during heating.

## 2. Experimental details

### 2.1. Materials

The fly ash used in this work was sourced from the Collie power station, Western Australia. The compositional information

**Table 1**

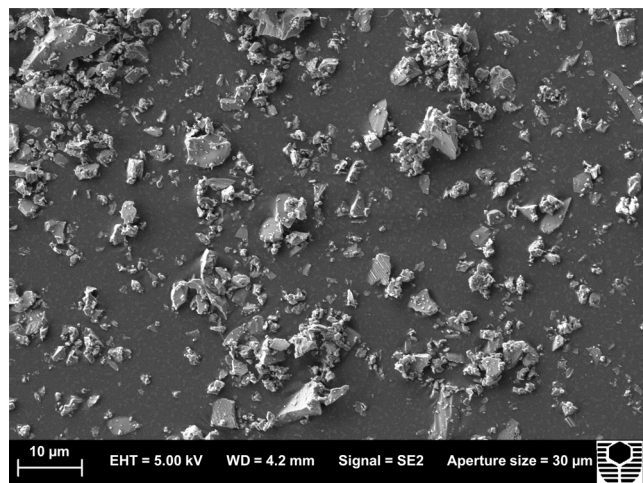
Composition of Collie fly ash. The numbers in brackets are the uncertainty in the last two significant figures of the adjacent value.

Oxide	Bulk composition (g/100 g)	Amorphous composition (g/100 g)
SiO <sub>2</sub>	50.03 (16)	24.84 (81)
Al <sub>2</sub> O <sub>3</sub>	24.93 (20)	13.03 (36)
Fe <sub>2</sub> O <sub>3</sub>	16.40 (4)	8.54 (45)
CaO	1.77 (10)	1.77 (10)
K <sub>2</sub> O	0.61 (8)	0.61 (8)
TiO <sub>2</sub>	1.37 (2)	1.37 (2)
MgO	1.29 (6)	1.29 (6)
Na <sub>2</sub> O	0.33 (10)	0.33 (10)
P <sub>2</sub> O <sub>5</sub>	1.50 (4)	1.50 (4)
SO <sub>3</sub>	0.33 (1)	0.33 (1)
BaO	0.34 (1)	0.34 (1)
Other	0.47 (12)	0.47 (12)
LOI	0.55	0.55
SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>	2.01	1.91
Si:Al (molar)	1.70	1.62

as determined by X-ray fluorescence (XRF) is shown in Table 1. The quoted uncertainty represents the estimate of the 95% confidence interval, based on the variation of repeat analysis of samples from the bulk material. The amorphous composition was determined by subtracting the crystalline content as determined by quantitative X-ray diffraction (QXRD) using a calcium fluoride internal standard from the total composition determined by XRF. XRD patterns were collected on a Bruker D8 Advanced diffractometer at 40 kV and 40 mA using Cu  $\alpha$  radiation. The data was collected over a  $2\theta$  range of 10–120° using  $2\theta$  steps of 0.01°, and a count time of 0.5 s. Rietveld modelling of the data was accomplished using Bruker AXS TOPAS version 4.2.

The two fillers investigated in this work are described in Table 2. The fillers were selected on the basis of their high melting points and uniform coefficient of thermal expansion (COTE) over the temperature range investigated. The morphology of the two fillers is shown in Figs. 1 and 2. The COTE value for  $\alpha$ -alumina over the range 0–1000 °C is  $8.1 \times 10^{-6} \text{ K}^{-1}$  [19].  $\alpha$ -Alumina [20] can be considered anisotropic with respect to thermal expansion. Wollastonite has an average COTE of  $6.5 \times 10^{-6} \text{ K}^{-1}$  over the range 25–800 °C [21].

The alkaline activating solutions were synthesised from sodium silicate, PQ-D A53, (PQ Australia) and sodium hydroxide pellets (Rowe Scientific, Australia). Sodium based activating was chosen to enable comparison with previous work and to produce economically viable materials. The composition of the PQ-D is 44.1 wt.% solids with a SiO<sub>2</sub>:Na<sub>2</sub>O modulus of 2.



**Fig. 1.** SEM micrograph of the alumina filler used in this study.

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