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Determination of the reactive component of fly ashes for geopolymer production using XRF and XRD

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ABSTRACT

Geopolymers are a class of versatile materials that have the potential for utilisation as a cement replacement, fireproof barriers, materials for high temperatures, and biological implant applications. This study investigated methods for determining the formulation for manufacturing geopolymers made with fly ash from coal-fired power stations. The accepted method of determining the formulation of geopolymers to get the desired matrix chemistry uses the bulk composition of the feedstock materials. This formulation method is widely used in investigations using feedstock materials that almost completely react during processing. It is widely considered that amorphous components of fly ash are the reactive components in the geopolymerisation reaction. However, quantification of the amorphous components is challenging and generally avoided with the concomitant problem that the formulation is far from optimum. For the work presented here, the composition of the amorphous part is determined accurately and this information utilised to synthesise geopolymers. The bulk composition is first determined using X-ray fluorescence spectroscopy (XRF) and then the amorphous composition determined using XRF and quantitative X-ray diffraction (QXRD). Formulating the mixture based on amorphous composition produced samples with a significantly higher compressive strength than those formulated using the bulk composition. Using the amorphous composition of fly ash produced geopolymers with similar physical properties to that of metakaolin geopolymers with the same targeted composition. We demonstrated a new quantitative formulation method that is superior to the accepted method.

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1. Introduction

Empirical formulation of geopolymers made with dehydroxylated kaolinite (metakaolin) have been investigated by many researchers [1–7]. The physical properties of the geopolymers depend primarily on the ratio of Si/Al, Na/Al and the water content [3,4]. Often these ratios are investigated indirectly for example, by varying the activation solution to solids ratio. However, even for metakaolin studies the bulk composition does not correlate to the micro chemistry of the geopolymer matrix [8]; an outcome of incomplete dissolution of Al and Si from metakaolin. The metakaolin geopolymer formulations optimised for maximum compressive strength is achieved when the nominal composition of Si/Al = 1.8 to 2.2 and Na/Al = 0.9 to 1.2 [4,5,9].

Fly ash is the fine particle residue transported by flue gas after the combustion of coal in a coal-fired power station. This fly ash is typically captured by electrostatic precipitators (ESP) or a bag filter. The chemical composition of the fly ash depends on the initial coal composition, and the mineralogical composition depends on the power station design and the power station operating conditions. Fly ash is typically an aluminosilicate with some iron and/or calcium oxides, with minor concentrations of Na, Mg, P, S, K, Ti, Sr and Ba. The chemical form of these elements can vary although typically fly ashes have quartz and mullite as major crystalline phases, and with usually 40–80 wt.% amorphous (non-crystalline) phases. The quartz in fly ash originates from both the source coal (primary quartz) and that formed during combustion (secondary quartz) [10]. The mullite forms during combustion by solid state reaction of decomposed clays and/or crystallization of the aluminosilicate melt [10,11]. When mullite forms by crystallization of a melt the Al/Si ratio has a greater variation than when it is formed by a solid state reaction [12].

Currently, the bulk composition of fly ash is widely used to formulate the mixture of fly ash based geopolymers. The properties of geopolymers can be varied by altering the Si/Al, Na/Al ratios and water content [13]. Many researchers also vary the 'activating solution' [14–16] which directly alters the mixture composition. These studies have shown that for different fly ashes, there is a disparity between the bulk ratios that achieve the maximum compressive strength. Despite this many studies have produced high quality fly ash geopolymers pastes, mortars and concrete. The for-

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mulation method as it stands is not robust and corrections for changes in fly ash bulk composition are usually not successful in maintaining the geopolymer properties. Factors that affect the fly ash reactivity are changes in combustion conditions, classification settings, coal composition and transport treatment (i.e. wet or dry).

Modelling of data from Pietersen et al. [11] showed that the dissolution of fly ash is dependent on the amorphous content at very high liquid to solid ratio (1000:1 by weight) in a strong sodium hydroxide solution [17]. Pietersen et al. concluded glass chemistry had little effect on the reactivity and that the dissolution rate of Al, Si and K was almost congruent. However Brouwers and van Eijk demonstrated that the shrinking core model could be used to describe Pietersen et al's system and in fact the dissolution of the outer hull (of fly ash spheres) is less reactive than the inner region due to different chemical composition [17]. With this in mind, it should be noted that dissolution of classified fly ash at a lower liquid to solid ratio (50:1) did not reveal a more reactive inner hull [18]. Geopolymer systems have much lower liquid to solid ratio and dissolution of fly ash in these conditions has been shown to be incongruent, with amorphous alumina being more soluble than amorphous silica [19] in specific cases. This is in contrast to geopolymer synthesised with large grain metakaolin, were the alumina was consistently less soluble than the silica [8]; when Na/Al $\geqslant$ 0.8.

Given the fly ash dissolution results [11,17] and the fly ash geopolymer microchemistry data [19] it is reasonable to assume the amorphous aluminosilicate component of fly ash is the reactive component. The assumption that the amorphous alumina and silica can be used for geopolymer mix design has been sporadically practiced in the literature, however usually with only one fly ash and very little attention is focused on the method [18,19]. The microchemistry of strength optimised fly ash geopolymers has previously been shown to have Si/Al and Na/Al ratio similar to that of metakaolin systems [15].

2. Materials and methods

The fly ashes chosen for this study are all available in bulk quantities and are widely utilised as supplementary cementitious material (SCM) for Portland and blended cements, and are reported to be suitable to produce geopolymer [20–22]. The fly ashes were sampled in 4th quarter 2007 from the Australian power stations in Collie (Western Australia), Port Augusta (South Australia) and Bayswater (New South Wales).

Fly ash extracted from the electrostatic precipitators (ESP) of Port Augusta's power station has a small particle size that does not need to be further classified. The other fly ashes in this study were classified prior to delivery with standard methods (with a cyclone device) to produce fine fly ash as defined by Australian Standards [23], which is 75 wt.% passing <45 μm. The 20 kg samples of fly ash supplied were riffle split with multiple riffle splitters to produce representative samples of different quantities, in particular ~3 g samples for all microanalysis (XRD, XRF, various synchrotron studies and electron microscopy), and ~100 g for geopolymer synthesis.

2.1. Determination of bulk composition

The bulk compositions of the fly ashes was measured by XRF and Loss on Ignition (LOI), which was determined by a commercial laboratory (Ultratrace Geoanalytical Laboratories, Canning Vale, WA, Australia), using 12:22 fusion beads, calibrated with relevant certified standards. Quoted uncertainties were estimated by the difference between measured certified standards and the relevant certified values. Loss on Ignition (LOI) has been determined between 105 and 1000 °C for 60 ± 5 min, with results being reported on a dry basis.

2.2. Determination of the crystalline composition

2.2.1. Quantitative phase analysis sample preparation

The fly ash samples for XRD were prepared by mixing a nominally dry weight of 3.0000 g of fly ash with 0.3333 g of Fluorite (CaF_2, Sigma–Aldrich >99.5%, powder ~325 mesh) as an internal standard. By using an internal standard the concentration of the crystalline phases can be determined on an absolute basis enabling the amorphous fraction to also be determined. This powder was then added to a McCrone micronising canister with 7 ml of laboratory grade ethanol and sintered alumina milling media and milled for 5.0 min. The suspension was then poured into a polypropylene dish and dried at 105 °C for 24 h. The dried powder was then brushed into a polypropylene vial, and sealed until analysis.

Synchrotron powder diffraction samples were loaded into 0.5 mm diameter borosilicate capillaries (GLAS, Schönwalde, Germany). The samples were loaded by placing a small quantity of sample in the opening of the capillary and vibrating the capillary with a soft brush on a rotary tool. The capillaries were then sealed with a butane microtorch.

2.2.2. Synchrotron based powder diffraction

The Powder Diffraction beamline 10-BM-1 at the Australian Synchrotron was used to collect the diffraction patterns of each fly ash sample. A double crystal monochromator was used to select the wavelength of 0.100073 nm, determined accurately by a Pawley Refinement of NIST SRM 660a (LaB_6) data. The beam was collimated to 7 mm width and 1 mm height. A MYTHEN detector system was used to collect the pattern from 10° to 90° 2θ. This detector system consists of 16 position sensitive detectors arranged such that there is a small gap between detector modules of 0.2°. To collect the data for these gaps the pattern was collected for 5.0 min and then the detector bank was moved 0.5° and the pattern measured for an additional 5.0 min. The script that was developed to splice the datasets is described elsewhere [24].

2.2.3. Selection of internal standards and micro-absorption considerations

The selection of the internal standard for quantitative X-ray diffraction of fly ashes is not trivial due to the Bragg peak overlaps and micro-absorption issues. Many internal standards were considered; the phases given the most consideration were corundum (Al_2O_3), zincite (ZnO), anatase (TiO_2), rutile (TiO_2), ilmenite ($FeTiO_3$), fluorite (CaF_2) and diamond (C). The corundum, anatase, rutile and ilmenite were ruled out as it was conceivable these phases could be present in the fly ash in trace quantities below the level of detection of preliminary laboratory XRD analysis.

Excessive micro-absorption differences result in biased quantitative phase abundances; this increases the measured abundances of strong absorbers and decreases the measured abundances for weak absorbers [25]. The degree of micro-absorption is related to the product of the mass attenuation coefficient, density and the particle diameter. The fly ashes have quartz, mullite and assorted iron oxides encapsulated in solid amorphous spheres, so the concept of particles in the sense of Brindley corrections is invalid. This does not mean micro-absorption is not a problem, quite the contrary, particularly if using Cu Kα where there is a major mismatch in mass attenuation coefficient between the aluminosilicates and the iron oxides. Fig. 1 shows the mass attenuation coefficient as a function of energy calculated using TOPAS version 4.2 (Bruker-AXS). This shows that for a wavelength of 0.100 nm (12.40 keV) fluorite (CaF_2) and rutile (TiO_2) are suitable because they result in the smallest difference in mass attenuation coefficients. The

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