Beneficiation of Collie fly ash for synthesis of geopolymer: Part 1 – Beneficiation

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HIGHLIGHTS

▶ Sieving of the ash leads to a noticeable reduction in quartz and carbon.
▶ Milling of the ash shows a significant increase in surface area and reactivity.
▶ Removal of crystalline iron from the ash results in a reduction in particle size.
▶ The majority of amorphous carbon in the fly ash is present as very fine particles.
▶ Quartz is present in the ash as primary quartz and secondary quartz.

ARTICLE INFO

ABSTRACT

Beneficiation of the fly ash was conducted in a three stage procedure using sieving, milling and magnetic separation to improve fly ash homogeneity and reactivity. Sieving was effective in reducing large carbon particles and free primary quartz content. Most of the carbon was found to be small and finely dispersed throughout the material, making it unfeasible to remove by sieving. Sieving in conjunction with milling increased surface area from 9.83 m^2/g to 10.7 m^2/g. Magnetic separation revealed that amorphous iron was not magnetic and the complete removal of crystalline iron phases is not possible without a robust separation technique. The removal of magnetic phases increased the surface area of the sieved and milled fly ash to 12.9 m^2/g.

The proportion of reactive amorphous material increased at each stage of beneficiation, resulting in increased reactivity. The increase in reactivity necessitated changes in solids:liquids ratio in order to maintain a workable geopolymer mixture which will be discussed in Part 2 of this set of papers. The outcomes from this research clearly identifies that different levels of fly ash beneficiation leads to different geopolymer properties, which in turn extend the range of applications for which geopolymers can be used.

1. Introduction

Geopolymer is a cementitious binder and is considered an environmentally friendly alternative to cement as it emits no CO_2 during production if ambient cured. Geopolymer production is a simple process that involves mixing an amorphous aluminosilicate feedstock with alkaline activating solution. In addition, this process is able to utilise low cost industrial by-products, such as blast furnace slag and fly ash as feedstock.

Although fly ash is suitable as a feedstock for synthesis of geopolymer, its inherent heterogeneity limits development of a general formulation for producing geopolymer. Beneficiation of fly ash can be considered a method for alleviating this limitation, leading to a more homogeneous geopolymer with improved properties.

Collie fly ash was selected for investigation. It is the most abundant fly ash in Western Australia and has been successfully used previously to make geopolymer concrete [1–4] and binder [5]. Rangan and co-workers demonstrated that Collie ash was suitable for synthesis of geopolymer binder, however their work was based on formulations derived only from XRF data. Detailed analysis (XRF/XRD) of Collie ash by Chen-Tan et al. [6] and Williams & van Riessen [7] clearly identified the amount and composition of the amorphous component of which a sizable fraction is iron oxide. This approach enabled determination of a more precise formulation with a concomitant increase in strength. Although the dual XRD/XRF analysis is robust and accurate, it does not enable an accurate prediction of the degree of reaction, as particle size and surface area is not taken into account. Therefore a parallel dissolution experiment was conducted, where the ash was dissolved in NaOH. Comparison of the analytical XRD/XRD approach with the dissolution experiment produced very similar figures for the reactive component, confirming the validity of the analytical methodology

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[6]. As XRD/XRF analysis is much quicker, this approach has been adopted for routine analysis of the composition of fly ash.

The rigorous analysis undertaken during the above exercise highlighted that beneficiation should be considered as a means of producing geopolymer with improved physical properties. The beneficiation steps investigated were sieving, grinding and magnetic separation. The aim of the project was to determine if beneficiation would lead to geopolymers with improved properties and if some of the by-products produced in the separation process could be treated as products in their own right [8].

2. Materials and methods

Fly ash from the Collie power station was retrieved from the electrostatic precipitator collection bags. The fly ash was not classified prior to bagging. A riffle splitter (Metal Craft) was utilised to ensure uniform and consistent sampling of fly ash from the bulk supply. The manual riffle splitter was used to sub-divide 20 kg of Collie fly ash into 1 kg allotments.

Particle size distribution of the fly ash was analysed by the Commonwealth Scientific and Industrial Research Organisation, Minerals Division (CSIRO Minerals) (http://www.csiro.au/places/Waterford.html). The fly ash was first de-agglomerated by suspension in ethanol and placing it in an ultrasonic bath. The specimens were analysed by a Malvern MasterSizer (MS2000), with a measuring range of 0.02–2000 μm utilising the Mie Scattering measurement principle [9].

BET analysis was conducted at CSIRO (http://www.csiro.au/places/Waterford.html). Powders were prepared by degassing at 100 °C and 100 mTorr for 3 h prior to analysis. Samples were analysed following ASTM C 1069 in a Micromeritics Tristar 3000, using nitrogen as the adsorbate gas at a temperature of 77.3 K.

XRF analysis was outsourced to Ultra Trace Geoanalytical Laboratories (http://www.ultratrace.com.au). Powdered samples were crushed and prepared using a glass fusion technique. The fusion beads were analysed using a Panalytical MagiX Pro spectrometer. Concentrations were derived from a comparison with known standards. Results were reported by Ultra Trace as elemental oxides with no uncertainty values. Uncertainty of the elemental values was taken as the standard deviation of repeated XRF analyses of either three or seven different samplings of the fly ash.

Powdered specimens for qualitative XRD were prepared by reducing the particle size to less than 10 μm in a McCrone Micronising Mill with sintered alumina media. Two grams of powder were milled with 10 mL of ethanol to minimise sample change due to percussive effects. Samples being prepared for quantitative analysis were spiked with 10 wt.% internal standard material (fluorite or zincite). Milling time was set at ten minutes.

A Bruker D8 Advance diffractometer was used for data collection. Quantitative data was collected from 10° to 120° 2θ with a 0.005° step size and scan time of 0.3 s per step. The Cu tube was set to a potential of 40 kV and tube current of 40 mA using Cu Kα radiation. The diffraction data was collected with a LynxEye detector. A knife edge collimator was introduced to reduce air scatter and samples were rotated during data collection. A Ni filter was used to eliminate k_β peaks. TOPAS 4.2 (Bruker) was utilised for Rietveld refinement with D8 Advance data.

The scanning electron microscopes utilised for image collection were a Philips XL30, Zeiss EVO 40XVP and Zeiss Neon 40EsB. The XL30 and EVO 40XVP instruments were equipped with a tungsten filament while the Zeiss Neon 40EsB was equipped with a field emission gun.

3. Results

3.1. Sieving

The as supplied ash, or unmodified ash (UFA), was sieved producing three sub-fractions with the <45 μm fraction being the dominate fraction (Table 1). Loss on ignition (LOI) for the whole sample was 2.06 wt.% which was ascribed to carbon. LOI values for the sub-fractions are presented in Table 1.

Quantitative XRD results for the sub-fractions of the ash are presented in Table 2. To accurately fit the quartz peaks using Rietveld refinement, two quartz phases were included in the refinement process. One quartz profile was utilised to represent the original quartz (primary quartz) present with the coal. The other quartz profile represented quartz formed during the combustion process which has the tendency to contain Al, Fe, Na or Ti substitution for Si.

For the fine fraction, also labelled sieved fly ash (SFA) there is less overall conversion of metakaolin to mullite and secondary

Table 1
Size fractions of Collie fly ash after sieving (uncertainties are one standard deviation of three analyses). Loss on ignition values (1050 °C) of different size fractions of Collie fly ash (uncertainties are one standard deviation of five samples).

Size fraction	Mass (wt.%)	LOI (wt.%)	Overall contribution of LOI (wt.%)
Coarse (>75 μm)	7.22 ± 0.05	5.59 ± 1.35	0.40 ± 0.10
Medium (⩽75 ⩾ 45 μm)	8.24 ± 0.05	1.36 ± 0.31	0.11 ± 0.03
Fine (<45 μm)	84.05 ± 2.19	1.71 ± 0.03	1.45 ± 0.03

Table 2
Quantitative XRD results.

Phase	Unmodified fly ash (UFA)	NM-UFA (wt.%)	Coarse fraction (wt.%)	Medium fraction (wt.%)	Fine fraction (SFA) (wt.%)	NM-SFA (wt.%)	MFA (wt.%)	NM-MFA (wt.%)
Amorphous	54.58 ± 1.03	53.28 ± 0.51	13.00 ± 3.96	30.61 ± 1.25	58.63 ± 0.79	57.00 ± 2.11	60.15 ± 0.47	60.10 ± 0.48
Hematite	1.64 ± 0.03	0.68 ± 0.04	0.61 ± 0.01	1.89 ± 0.06	1.82 ± 0.06	0.75 ± 0.06	1.94 ± 0.05	0.96 ± 0.04
Maghemite	3.45 ± 0.10	1.10 ± 0.20	1.67 ± 0.03	3.97 ± 0.10	3.68 ± 0.12	1.00 ± 0.07	3.61 ± 0.17	1.56 ± 0.22
Magnetite	2.33 ± 0.10	0.39 ± 0.10	1.42 ± 0.12	3.95 ± 0.03	2.33 ± 0.04	0.42 ± 0.04	2.37 ± 0.10	0.59 ± 0.12
Mullite	16.2 ± 0.15	19.86 ± 0.18	9.38 ± 0.27	18.24 ± 0.33	17.15 ± 0.30	20.74 ± 0.80	16.81 ± 0.17	19.01 ± 0.19
Quartz (primary)	12.16 ± 0.71	13.57 ± 0.28	39.75 ± 2.21	25.13 ± 0.86	7.27 ± 0.22	9.70 ± 0.53	7.42 ± 0.22	9.15 ± 0.17
Quartz (secondary)	9.65 ± 0.33	11.12 ± 0.10	34.20 ± 1.36	16.21 ± 0.72	9.11 ± 0.52	10.38 ± 0.69	7.68 ± 0.17	8.64 ± 0.27
Carbon	2.06 ± 0.07		5.59 ± 1.35	1.36 ± 0.31	1.71 ± 0.03			