Toward an indexing approach to evaluate fly ashes for geopolymer manufacture

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ABSTRACT

Variations between fly ashes can lead to significant differences in the geopolymers derived from them, in both microstructural and mechanical properties. This study assesses the effect of physical, crystallographic and chemical characteristics of fly ash on geopolymerisation performance and the strength of the resulting binders. Physical and glass chemistry factors are combined to develop a comprehensive index to evaluate the suitability of fly ashes for the production of high-strength geopolymers. An equation for this index is proposed, developed using five typical low-calcium fly ashes and then validated against a further eight literature datasets, showing a good relationship between the ranking order of the calculated index and the compressive strengths of geopolymer pastes produced with comparable activator and paste workability. This index can be used to screen the source materials, which is of significant value in moving alkali activated cements towards acceptance in practice.

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1. Introduction

With demand driven by environmental protection and waste utilisation, alkali-activated aluminosilicate materials, also known as geopolymers, have been developed rapidly in the last two decades and are increasingly regarded as promising green alternatives to Portland-based cements [1]. Accordingly, geopolymers based on alkali activation of fly ash have been extensively studied. Fly ash-based geopolymer technology is considered particularly attractive for commercialisation in areas of the world where this precursor is available in large volumes including Australia, China and the USA. Its lower activator requirement, compared to metakaolin, which is another type of widely used raw material, means that fly ash-based geopolymer can be produced at a low cost.

Some demonstration projects have been constructed using geopolymer concretes made from alkali activated fly ash blended with certain proportions of slag [2]. However, large-scale manufacture of fly ash-based geopolymer still progresses slowly and faces some technical and regulatory obstacles [3]. Among these, the inconsistent properties of fly ash (between sources, and from time to time from a single source)

may be the most critical technical issue hindering large-scale deployment. Variations in the chemical compositions of coal sources, and the details of the combustion processes applied in different facilities worldwide, result in significant differences in terms of the chemical and physical characteristics of the resulting fly ashes. These variations lead to varying properties and performance levels in the geopolymers produced, as has been demonstrated using fly ashes obtained from different sources worldwide [4–6]. This hinders the acceptance of geopolymer concrete by the civil engineering and construction industries, as the relationship between mix design parameters and performance is not as readily predictable as is the case for Portland cement-based systems, which necessitates extensive laboratory testing prior to the use of any particular geopolymer mix design, and means that ongoing quality control throughout a production run is essential. To solve this problem, it is necessary to construct effective assessment methods to determine the performance of fly ashes in geopolymer mixes and predict their likely strength development based on readily-assessed material parameters.

In previous studies [4–6], it has been found that key factors affecting the compressive strength development of fly ash-based geopolymers include particle size distribution, the content of glassy phases and the content of glass network modifying species (mainly alkali and alkali earth metals). The avoidance of excessive unburnt carbon content is also important [7], but the regulatory loss on ignition limits which are imposed on fly ashes sold for blending with cement and concrete is likely to be sufficient to ensure that this parameter is not problematic in

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their use in geopolymerisation. It may thus be expected that a fly ash with small particle size, high glass content and high network modifier content would yield high compressive strength of the derived geopolymer. However, a model built from a single parameter is not sufficient to correlate with the mechanical performance of the resulting geopolymer [5,8]. For example, the Class C fly ash 'BY' used by Diaz et al. [5] showed the fastest setting (1.5 min) in alkali-activation among five ashes tested by those authors because of its high content of CaO (22.45%) and the finest particles, but resulted in the formation of a geopolymer with the second highest compressive strength; in comparison, the fly ash 'ML', which had the second-highest amount of CaO and the second-highest amount of glassy phases, exhibited the highest geopolymer strength.

More fundamental understanding is expected to come from detailed analysis of the content and chemistry of the glassy phases in fly ashes, but this is complicated by the heterogeneity of the glasses, within and between particles even in ash from a single source. By using quantitative X-ray diffractometry (XRD), electron microscopy and selective dissolution techniques, it is possible to determine the quantity and composition of the glassy phases in a fly ash [9–14]. The network modifier content and Si/Al ratio in the glassy fraction are considered to be the two critical factors that play important roles in determining the dissolution of fly ash [15] in geopolymerisation, and these parameters have also been linked into a single descriptor through the introduction of 'optical basicity' as a proposed (but not yet widely used) measure of fly ash chemistry [16]. Fe is another important element present in many fly ashes and it brings more complexity for the understanding of geopolymerisation, as its role in the glass dissolution and gel formation processes is yet to be fully defined [17–19].

There is thus an evident need for a comprehensive index, considering not only chemical but also physical properties of fly ash, to be able to effectively evaluate the 'grade' of a fly ash in terms of its suitability for geopolymer manufacture, where predictable and consistent performance is critical in the absence of any performance-buffering effect from a manufactured Portland cement clinker component as is the case for blended cements. In this study, we demonstrate one such indexing concept, enabling effective evaluation of the suitability of fly ashes for the manufacturing of high strength geopolymers. Physical, chemical and crystallographic properties of five typical low-calcium Australian fly ashes are characterised and used to develop a reactivity index from theoretical grounds, and the effects of these parameters on geopolymer formation are examined. In combination with the understanding of glass chemistry which is available in the literature, a comprehensive index to correlate the characteristics of fly ash with the strength of geopolymer products is proposed for the first time, and validated against a broader set of literature data for low-calcium fly ashes reacting to form geopolymers.

2. Experimental programme

2.1. Materials

Five Australian fly ashes, obtained from Gladstone, Millmerran, Callide, Eraring and Tarong power stations, were used in this study, and are denoted as A, B, C, D and E for brevity. Fly ashes from these power stations, except for Millmerran, have been studied previously in work including [4,14,18,20], and relevant information can be obtained from those studies for comparison. An alkaline activating solution was formulated by blending a commercial sodium silicate solution (Na_2O = 14.7% (mass), SiO_2 = 29.4%, D-Grade™, PQ Australia) with 12 M NaOH solution to reach the desired modulus (molar ratio SiO_2:Na_2O) of 1.0 and concentration of 36.7 wt.% of (Na_2O + SiO_2). This activator was allowed to equilibrate to room temperature prior to use. Deionised water was used throughout all experiments.

2.2. Fly ash characterisation

The key parameters of the fly ashes include particle size distribution, specific surface area (SSA), particle density, particle packing density, bulk composition and mineralogical composition. Particle size distributions of the five samples were determined using a laser diffraction particle size analyser (PSA, Malvern Mastersizer 2000). SSA was determined from the PSA results assuming spherical particles (geometric surface area), and was also measured by the Brunauer–Emmett–Teller (BET) method using nitrogen sorption on a Micromeritics TriStar II 3020 instrument (accessible surface area). Particle density was determined by the Archimedes method, using acetone and a volumetric flask. Particle packing density was simply determined as the ratio of weight to volume of each ash in a graduated container following 1 min of shaking by hand. Three replicate tests were conducted for each fly ash to obtain an average particle packing density. The mass loss which takes place upon heating was determined by thermogravimetric analysis (TGA) using a TA Q500 instrument under ambient air, heating at 10 °C/min from room temperature to 800 °C. The content of carbonaceous particles (which will include organics as well as carbonates) was defined as the mass loss at higher than 450 °C, where the contribution to loss on ignition below this temperature is attributed to superficial hydration.

Bulk fly ash composition was determined using an ARL-9800 X-ray fluorescence (XRF) instrument (Thermo Scientific), including loss on ignition analysis at 1000 °C in air. The mineralogical components, including crystalline and glassy phases, in each fly ash were identified by XRD and quantified by Rietveld refinement. The XRD data were collected using an ARL 9900 Series X-ray workstation (Thermo Scientific) with Co Kα radiation, operated at 40 kV and 40 mA, with a step size of 0.02° and count time 4 s/step from 8° to 80° 2θ. Each fly ash sample, without any classification or grinding, was mixed with 20% corundum (α–Al_2O_3 ≥ 99.99%, Aladdin), as an internal standard. The error of this quantitative XRD technique is assessed by comparing the quantities of each phases determined at three levels of internal standards (20%, 15% and 10%). The morphologies of fly ash samples and dried geopolymer samples, coated with gold, were analysed using a JEOL JCM-6000 scanning electron microscope (SEM) at high vacuum, with 15 kV accelerating voltage. To better understand the composition distribution (particularly for Fe and Ti) of glass and crystalline phases, selected fly ash samples were also etched with 1 M NaOH solution and analysed with energy dispersive spectroscopy (EDS).

2.3. Geopolymer synthesis and test procedure

Pastes were formulated initially at a target activator/ash ratio of 0.39 (Table 1). At this ratio the mixtures based on ashes A and C exhibited favourable workability; however, because of the varying particle properties of the ashes, pastes B, D and E required small amounts of additional water during mixing to achieve similar workability, as measured by using a minislump test. The addition of water has changed the concentrations of the dissolved activator components but not the modulus of the activator or the dose of alkalis with respect to the mass of fly ash (Table 1). The activator concentration is a parameter that can affect the geopolymerisation rate at early age, but will not necessarily change the total reaction extent, as indicated by the equivalence of the total heat released by systems with the same Na_2O content at differing water contents in calorimetric testing [21]. To supplement these tests and enable comparisons to be conducted also on the basis of constant activator chemistry, a second set of pastes were prepared by activation of fly ashes A, B and E with an activator mixed with water to match the diluted activator (activator plus water) used for ash D, at liquid/solid ratios yielding comparable workability for each ash (samples A_L, B_L and E_L, Table 1). There are thus two sets of samples available for direct comparison: samples A, B, C, D and E are formulated at constant activator (Na_2O + SiO_2) dose and modulus but with differing activator