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Effect of synthesis parameters on the performance of alkali-activated non-conformant EN 450 pulverised fuel ash

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HIGHLIGHTS

- EN 450 non-conformant PFAs can be used to produce geopolymers.
- Alkali concentration is an important synthesis parameter.
- Excess alkalis increase carbonation shrinkage and low strength.

ARTICLE INFO

ABSTRACT

The fly ash reported in this paper is coarser than conventional pulverised fuel ash (PFA), with loss on ignition (LOI) exceeding 10.8%. Consequently, it is precluded from being used as a supplementary cementitious material (SCM) according to EN 450 and disposed in landfills. Alkali-activation of such PFAs is considered here. Three concentrations of sodium hydroxide (NaOH) were separately blended with water glass at different ratios to modify the silica modulus. Heat of reaction, setting time, compressive strength and drying shrinkage were investigated as a function of activator composition. Specimens were either cured at room temperature or hydro-thermally treated at 75 °C for five hours. The results show that by optimizing the activator composition, a binder with a 28 day compressive strength of 25 MPa can be synthesised from such PFAs even at room temperature. Among the activator parameters, the alkali content was observed to be most influential.

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1. Introduction

Alkali-activated binders present a low-carbon alternative to Portland cement [1]. This class of binders are obtained from the reaction between alumina-silicate feedstock and concentrated solutions of alkali hydroxides [2,3], silicates [4], sulphates [5], carbonates [6] or combinations thereof [7,8]. An overview of the mechanism responsible for the transformation of the initial constituent materials into a binder has been extensively reported [9,10]. At higher pH, reactive alumina and silicates dissolve from the feedstock and when speciation equilibrium conditions are attained, the species precipitate into gels. Progressive interconnectivity of precipitated species, reorganization and condensation lead to a solid binder phase.

The parameters which influence the fresh and hardened properties of alkali-activated binders fall into two categories. That is, those inherent within the constituent materials, and the externally applied conditions. With regards to the intrinsic parameters, a variety of activators have been studied [11–14], as have a variety of feedstock materials [13–15]. The proportioning of these materials are system specific [16,17] and consequently determine the properties of the binder produced [3]. The effect of silica moduli [4,18,19], silicate to alumina [20–22] and water to silicate ratios have all been explored. However, mechanical performance is usually related to the silica modulus [23,24]. Recent studies have suggested that the amorphous silica to alumina ratio (SiO_2/Al_2O_3) also plays a significant role on the early age properties [25]. The optimum SiO_2/Al_2O_3 ratio however depends on the calcium content of the feedstock [26,27]. It therefore follows that a generalised mix formulation in these binders does not exist, thus necessitating the need to optimize the activator composition for every feedstock.

A range of alumina-silicate source materials for the synthesis of this class of binders have been explored in the literature [28–31]. Most of the explored feedstock however requires thermal or mechanical processing in order to obtain reasonable performance

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[32–37]. As a result, pulverised fuel ash (PFA), an industrial by-product which can be used directly will remain a popular and rather cheaper option. By virtue of being an industrial waste, the properties of PFA are dependent on coal source [25], pulverisation and combustion conditions [38,39] which are often tailored to maximize energy output rather than the quality of the ash. Technology and control of environmental pollution also dictates the ash collection method which also impacts on the quality of the PFA [40]. This leads to wide compositional variability, even from a single power stations [41,42].

The variability in PFAs even from the same source can restrict their use as SCMs. For example, the European norm EN 450-1 imposes compositional and physical requirements for PFA as SCMs; unburnt carbon content below 9%, as well as a maximum content of 40% coarser than 45 μ [43]. Non-conformant PFAs end up as landfill wastes at a cost to power generators. Previously reported alkali-activated PFAs offer potential technical advantages. However, the PFA feedstock mostly conforms to the EN 450 criteria [3,44–48] thus competing with those used as SCMs in composite cements. The suitability of non conformant PFA for geopolymer synthesis has not been studied previously and constitutes the objective of this paper.

2. Experimental details

2.1. Materials

Unconditioned PFA obtained directly from electrostatic precipitating hubs from a UK Power station was used for this study. The X-ray fluorescence (XRF) composition and the particle size distribution obtained through Malvern Mastersizer are shown in Table 1 and Fig. 1 respectively.

Iso-propanol was used as dispersant for the PSD measurement and the Fraunhofer method was implemented for data evaluation. The LOI was separately determined according to the method in EN 196-2 hence the sum of the oxide compositions including the LOI exceeding 100%.

Activators for the study were formulated from water glass solution and laboratory grade sodium hydroxide pellets (98% purity). The water glass solution composed of $8.5 \pm 0.3\%$ Na_2O and $27.8 \pm 0.5\%$ SiO_2. The viscosity and specific gravity were 70–120 MPa.s and 1.385 g/cm^3 respectively. Three concentrations of sodium hydroxide solutions (8, 15 and 20 M) were added at different levels to modify the silica modulus [4]. The activator composition and calculated molar ratios are shown in Table 2. The choice of the investigated activator composition range was based on the varied optimal ranges reported in the literature [49].

2.2. Sample preparation and testing

Isothermal conduction calorimetry was conducted on an 8-channel TAM Air calorimeter. 6.0 g of PFA and 3.0 g of the activating solutions were weighed and kept in the calorimeter until a stable baseline was attained. The activating solution was subsequently injected and then mixed in situ.

Setting time was measured on paste samples according to BS EN 196-3 using the Vicat apparatus. The entire test setup was submerged under water as prescribed in the norm. The reported setting times are average of three measurements. Mixing procedure for setting time, shrinkage and compressive strength testing were based on the recommendations of BS EN 196-1. The activating solution to feedstock ratio was maintained at 0.5. This was established from the consistency tests during the scoping studies.

Compressive strength and drying shrinkage were measured on mortar samples in replicates of three. The mortar specimens were prepared with 1:1:0.5 PFA/sand/activator ratios. The mix ratio was adopted in order to maintain the activating solution/PFA ratio at the same level as that which was used for the setting time and calorimetry measurements. The specimens for strength test were 50 mm cubes. Shrinkage test was based on BS ISO 1920-8:2009 but using 40 × 40 × 160 mm mortar prisms and demountable mechanical (i.e. demec) gauge studs. Measurements commenced 1 day after the relevant curing method. The demec points were attached on all four longitudinal sides of the test specimens using the polyester-
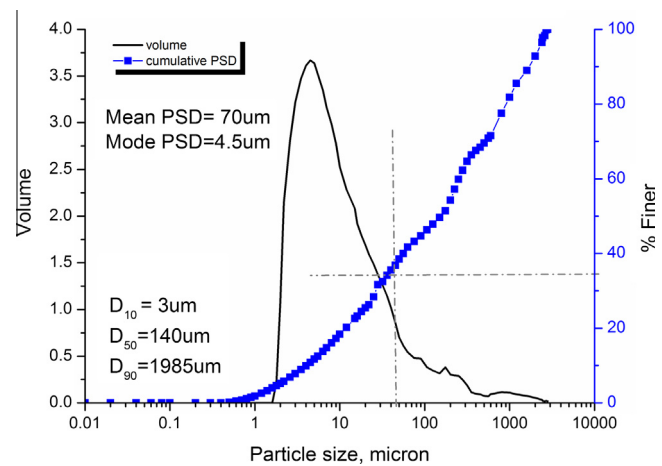

Fig. 1. Particle size distribution of the PFA under investigation.

based adhesive, chemical metal. Autogenous shrinkage (Auto) was taken as the shrinkage on samples sealed with flash band and monitored from 1 day. Two curing regimes were assessed; continuous curing at room temperature (RT) and hydrothermally treated at 75 °C for five hours (75), as performed elsewhere [50]. The hydro-thermal curing was achieved by introducing the moulds in a pan which was half-filled with water and covered with an aluminium foil.

3. Results and discussion

3.1. Reaction kinetics

The data presented here is limited to 20 °C because it was not possible to perform hydrothermal curing in a calorimeter. Previous studies also converge on enhanced kinetics of reaction at elevated temperatures [3,51,52]. The objective here is therefore to clarify the influence of alkali concentration and dosage on the reactivity and kinetics at ambient temperature.

The kinetics of early stage reactions as a function of activator composition are shown in Fig. 2(a–c). In all formulations, the heat flow was characterized by a single exothermic peak which occurred within 20 min after mixing. A short induction stage can be seen in the 8 M NaOH mixes (Fig. 2a); but no appreciable induction was observed in the 15 M and 20 M mixes. The end of the induction period which was about 3 min in the present study marked the onset of the dissolution of silicate and aluminate species [24] from the PFA. This being distinct in the 8 M NaOH activated mixes can be explained by the differences in the aluminosilicate dissolution rate [53,54]. The 8 M NaOH activated mixes contained more water but lower hydroxyl ions compared to the 15 M and 20 M NaOH blends. Consequently, the increased PFA/hydroxyl ion ratio retards dissolution. This is consistent with the data from leaching experiments reported elsewhere [55].

At a given NaOH molarity, an inverse relationship was noticed between the silicate dosage and the rate of reaction. This effect was less distinct in the 8 M NaOH mixes except at silica moduli of 2.6 and 3.1. Comparison between Fig. 2a and b depicts the significance of the alkali concentration which was used to modify the silica modulus of water glass. The rate of reaction was accelerated with increasing alkali concentration. However, this seems to reach a maximum at 15 M NaOH. Beyond this, differences between 15

Table 1
XRF composition of the PFA under investigation.

Oxide	SiO_2	Al_2O_3	Fe_2O	CaO	MgO	Na_2O	K_2O	TiO_2	SO_2	LOI
%	51.42	24.33	13.10	4.06	2.16	0.85	2.45	1.15	0.52	10.78