



Modification of phase evolution in alkali-activated blast furnace slag by the incorporation of fly ash



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ABSTRACT

The microstructural evolution of alkali-activated binders based on blast furnace slag, fly ash and their blends during the first six months of sealed curing is assessed. The nature of the main binding gels in these blends shows distinct characteristics with respect to binder composition. It is evident that the incorporation of fly ash as an additional source of alumina and silica, but not calcium, in activated slag binders affects the mechanism and rate of formation of the main binding gels. The rate of formation of the main binding gel phases depends strongly on fly ash content. Pastes based solely on silicate-activated slag show a structure dominated by a C–A–S–H type gel, while silicate-activated fly ash are dominated by N–A–S–H ‘geopolymer’ gel. Blended slag-fly ash binders can demonstrate the formation of co-existing C–A–S–H and geopolymer gels, which are clearly distinguishable at earlier age when the binder contains no more than 75 wt.% fly ash. The separation in chemistry between different regions of the gel becomes less distinct at longer age. With a slower overall reaction rate, a 1:1 slag:fly ash system shares more microstructural features with a slag-based binder than a fly ash-based binder, indicating the strong influence of calcium on the gel chemistry, particularly with regard to the bound water environments within the gel. However, in systems with similar or lower slag content, a hybrid type gel described as N–(C)–A–S–H is also identified, as part of the Ca released by slag dissolution is incorporated into the N–A–S–H type gel resulting from fly ash activation. Fly ash-based binders exhibit a slower reaction compared to activated-slag pastes, but extended times of curing promote the formation of more cross-linked binding products and a denser microstructure. This mechanism is slower for samples with lower slag content, emphasizing the correct selection of binder proportions in promoting a well-densified, durable solid microstructure.

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1. Introduction

Climate change is a global issue, and many countries are committing to reduce their emissions of greenhouse gases to reduce their environmental impact. The fact that the production of one tonne of Portland cement generates almost one tonne of carbon dioxide leads to the urgent need to search for alternative materials for the partial or total replacement of Portland cement with reduced carbon footprint [1]. This has been one of the main drivers for the development of alternative clinker-free binders, such as alkali-activated binders including ‘geopolymers’, which are

produced at room temperature through the reaction between an aluminosilicate precursor and an alkaline activator, to promote the dissolution and consequent polycondensation of binding phases to form a hardened material with good mechanical strength and durability [2,3].

Fly ash and blast furnace slag are the most popular choices as main raw materials in the production of alkali-activated materials, and their activation has been extensively studied over the past decades [4–9]. Marked structural, mechanical and physical differences have been identified in activated binders using precursors from different sources, as a consequence of the chemical and physical differences between slag and fly ash precursors and the influences of different activator concentrations and chemistries, and the microstructures of alkali-activated slag and of fly ash geopolymers have been extensively studied in systems based on sole precursors. The alkali activation of slag involves the dissolution

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of calcium and participation of Al to form a C-(A)-S-H type gel [10–12], promoting the development of high mechanical strength and durability in these systems [13–16]. On the other hand, strength development in alkali-activated aluminosilicate binders is provided by the formation of a three dimensional “N-A-S-H” type gel i.e. a sodium aluminosilicate gel forms as the main reaction product in these systems [17,18].

The use of slag and fly ash together to form an alkali-activated binder will generally lead to formation of a high amount of tetra-coordinated Al charge-balanced by Na, and binder gels in the hydrated $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. The nature of the main type of gel formed when both precursors are activated depends on various factors such as activator type and concentration, and the relative amounts of fly ash and slag. In general, dissolution of slag and fly ash upon alkali activation can produce a higher degree of cross-linking in binder systems consisting of both C-A-S-H and N-A-S-H gels. Lloyd [19], assessing the structure of different activated slag/fly ash blends, identified that increasing the amount of slag as a calcium source will lead to the formation of C-S-H products with certain degrees of aluminum substitution, depending on the availability of this element in the fly ash and slag. Escalante García et al. [20] identified an optimal activator modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio) of around 1.0–1.5 for a 1:1 blend of fly ash and slag, as a consequence of the scope for coexistence of both C-S-H and N-A-S-H in the system. Kumar et al. investigated the effect of slag replacement in fly ash geopolymers in the kinetics of reaction, finding that the C-S-H gel dominates the reaction products, co-existing with aluminosilicate gels, resulting in improved setting properties and higher compressive strength with slag addition [21,22]. The X-ray microtomography data of Provis et al. [23] show a similar dominance of slag on a microstructural level, as the 1:1 blend of fly ash and slag in that investigation displayed trends in porosity which were more similar to a slag-based binder than a fly ash-based binder. Microstructural observation of younger-age pastes by Yang et al. [24] also showed that partial slag substitution in sodium hydroxide-based fly ash geopolymers improves strength and affects the reaction mechanism controlling the formation of the main binding gels.

Despite these previous studies, an in-depth understanding of the mechanism of incorporation of fly ash in activated slag binders, and the associated effects on longer term evolution of microstructure, is still lacking. The knowledge of microstructural development of activated binders using fly ash and slag as precursors is limited to relatively immature samples, while it is known that changes in the binder phase can proceed even at an advanced curing age [25]. The dissolution of fly ash in an activated slag binder may take longer, and this justifies investigation well beyond the most commonly studied curing age of 28 days. It is vital to understand the evolution of phases over time for various mix proportions of fly ash and slag in order to design for specific strengths or to ensure durability. Therefore, this study will characterize the microstructural changes taking place in alkali-activated slag/fly ash binders up to the age of 180 days, using X-ray diffraction, infrared spectroscopy, thermogravimetry and scanning electron microscopy.

2. Experimental methods

2.1. Materials

The geopolymer precursors used in this investigation were a fly ash (FA), Class F according to ASTM C 618, from Bayswater Power Station, New South Wales, Australia, and a granulated blast furnace slag (GBFS) supplied by Zeobond Pty Ltd, Australia. The oxide compositions of the precursors are given in Table 1. It is notable that

the fly ash used is very low in calcium, which enables the development and analysis of calcium-free gel structures in the fly ash-based binder systems. The GBFS has a density of 2800 kg/m^3 and a d_{50} of $15 \mu\text{m}$, while the fly ash has a density of 2200 kg/m^3 and a d_{50} of $12 \mu\text{m}$.

The alkali activator was prepared by dissolution of a solid anhydrous sodium metasilicate (49.1 wt.% SiO_2 and 50.9 wt.% Na_2O , supplied by Zeobond Pty. Ltd.) in the mix water, which was then allowed to cool to room temperature prior to preparation of the specimens. The activator doses used were 8 wt.% or 12 wt.%, by total mass of precursor (i.e., 8 g or 12 g Na_2SiO_3 per 100 g FA + GBFS), as described in Table 2. It should be noted that setting and hardening did not occur satisfactorily for samples containing $\geq 75\%$ fly ash at lower concentrations of metasilicate, and therefore a higher activator dose was required to achieve satisfactory strength development in the binders containing this amount of fly ash. All samples were formulated with a water/binder ratio of 0.40, and cured in sealed polypropylene tubes at 30°C to provide a controlled curing environment under which the material would harden sufficiently rapidly, but which is not far removed from the ambient conditions prevailing in many parts of the world, and so is relevant for practical purposes.

2.2. Analytical techniques

Microstructural and chemical analysis were performed on paste samples after 14, 28, 90 and 180 days of curing, through:

- X-ray diffraction (XRD) using a Bruker D8 Advance instrument, scanning from 5° to $65^\circ 2\theta$, with a 0.02° step size and 2 s/step count time.
- Fourier transform infrared (FTIR) spectroscopy, using the KBr pellet method in a Bruker Tensor 27 spectrometer, scanning 32 times from 4000 to 400 cm^{-1} at 4 cm^{-1} resolution.
- Thermogravimetry (TG), in a PerkinElmer Diamond instrument. Samples were crushed, transferred immediately to an alumina crucible, held under isothermal conditions for 60 min at 40°C to equilibrate, and then heated $40\text{--}1000^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$ in a nitrogen environment at $200 \text{ mL}/\text{min}$ purge rate.
- Environmental scanning electron microscopy (ESEM) with energy dispersive X-ray (EDX) analysis, at an accelerating voltage of 15 kV using an FEI Quanta ESEM instrument. Paste samples were sectioned, and polished up to $1 \mu\text{m}$ surface fineness using diamond paste. Between 35 and 40 data points were collected for the elemental analysis of each sample.

3. Results and discussion

3.1. X-ray diffraction of raw materials and alkali-activated binders

The X-ray diffractograms of the anhydrous fly ash and slag are shown in Fig. 1. The unreacted fly ash shows, as main crystalline phases, quartz (SiO_2 , Powder Diffraction File (PDF) # 01-079-1910), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$, PDF# 00-015-0776), hematite (Fe_2O_3 , PDF# 00-033-0664), and maghemite (Fe_2O_3 , PDF# 00-039-1346). The unreacted slag shows as main crystalline phases a small amount of calcium carbonate (CaCO_3) in its three polymorphs (calcite, PDF# 01-071-3699; aragonite, PDF# 01-076-0606; and vaterite, PDF# 01-075-9356), associated with the superficial weathering of the slag during storage, and gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, PDF# 00-033-0311). The gypsum in the slag is likely to be associated with the milling process of the granulated slag, which is conducted in a facility used for Portland cement production. Both fly ash and slag also show a broad ‘hump’ feature due to the amorphous component, in the case of the fly ash between $2\theta = 15^\circ$ and 35° , and in the unreacted slag between $2\theta = 25^\circ$ and 35° . The

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