Upcycling of cementitious wastes in one-part alkaline cement binders

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Abstract. Cementitious wastes generate at an increasing rate and are generally disposed of in landfills, creating harmful environmental impacts. Therefore, enhancing potential pathways to recycle such wastes is critical. In this study, two ways of introducing cementitious wastes in one-part alkaline cement binders (ACBs) are presented: as solid precursors and as activators. A mixture of fly ash and blast furnace slag as the solid precursors and a blend of thermally treated sodium hydroxide and waste glass as the alkali activator were used to cast ACBs by just adding water similar to ordinary Portland cement. Glass powder-based activator showed 70% of efficiency in creating crystalline sodium silicate which dissolves in the binder phase to enhance the production of hydration products. Reasonable compressive strengths of the hardened paste were reported resulting in a dense microstructure with the curing age. Therefore, in this study, the increasing involvement of cementitious wastes in one-part ACBs is confirmed.

Keywords: cementitious wastes, one-part alkaline cement binders, partial activator, strength and microstructure.

1. Introduction

Alkaline cement has become a vast technology over time and can replace ordinary Portland cement overcoming its inherent disadvantages. Recent studies have pointed out its capability to consume cementitious wastes and hence favours much attention in waste recycling points of view. ACBs mainly consisted of two components: solid precursors and activators. Materials with significant silicon, aluminium, or calcium minerals serve as solid precursors with several combinations. Coal ashes, metal slags, municipal solid waste incinerator ashes, mine tailings, construction debris, waste glass are the most commonly reported solid precursors in ACBs [1]. Commercial alkali hydroxides and alkali silicates, both in liquid and solid forms, are widely used as activators in ACBs. In the meantime, few researchers studied the potential use of waste materials such as rice husk ash and waste glass as alkali activators of ACBs [2, 3]. Depend on the physical form of the activator: solid or liquid, ACBs are mainly divided into two categories: one-part and two-part ACBs, respectively. However, two-part ACBs, consisting of solid precursors and liquid activators, have several drawbacks over one-part ACBs. One-part ACBs use both precursors and activators in solid form and cast similar to ordinary Portland cement (OPC) by Simply adding water. Solid activators are preferred over liquid ones because activators in liquid form require serious attention on handling, transporting and storing aspects [4]. The activator solutions such as a blend of commercial sodium hydroxide (NaOH) and sodium silicate (Na2SiO3) with...
Na$_2$O/SiO$_2$ = 1 are considered as corrosive materials [5]. Therefore, liquid activators restrict the cementing applications in in-situ conditions, especially in bulk production.

In most of the studies, commercially available alkali hydroxides and silicates have been used as the solid activator in one-part systems, although they have used cementitious wastes as solid precursors [6]. These commercial activators provide high alkaline conditions, pH > 12, to accelerate the dissolution of solid precursors. However, it is challenging to create high alkaline conditions using the activators with waste materials alone. On the other hand, the initial dissolution of solid precursors is relatively low in one-part binders compared to two-part binders since the liquid alkaline solutions provide better alkaline media in two-part systems [7]. In one-part systems, dissolution of activator in water is the most critical step to create alkaline conditions to subsequent leach out of minerals of solid precursors. Hence, it is advisable to partially replace the solid activator with potential waste blended with a commercial alkali supplier to enhance the initial dissolution of aluminosilicate precursors. However, those commercial activators, especially alkali silicates, have significant adverse effects on the cost, energy and emission points of view [8]. Moreover, a limited number of studies are available regarding the one-part ACBs consisting of waste materials that can substitute for the solid activator. Therefore, it is necessary to incorporate potential waste materials into the activator of one-part ACBs, enhancing the recycling rate of such types of wastes. This study mainly focuses on the possible inclusion of waste glass powder to replace commercial alkali silicates in the solid activator. Finally, it is expected to increase the involvement of potential waste materials in one-part ACBs for both activator and precursors by minimizing the inclusion of commercial materials.

2. Experimental work

2.1. Materials and mix design

Class F fly ash, and ground granulated blast furnace slag (GGBFS) were sourced from Independent Cement & Lime Pty Ltd, Australia. The crushed glass was purchased from Let’s Clean Pty Ltd, Australia and further pulverized into a powder using a laboratory-grade ring mill. NaOH micro-pearls were obtained from Redox Pty Ltd, Australia. The chemical compositions with the mean particle diameters of the raw materials are shown in Table 1.

| Wt.% | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | K$_2$O | Na$_2$O | SO$_3$ | P$_2$O$_5$ | TiO$_2$ | LOI$^a$ | D$_{50}$ $^b$ |
|------|---------|-------------|-------------|-----|-----|-------|--------|--------|----------|--------|---------|----------|
| FA   | 62.7    | 27.1        | 2.6         | 2.1 | 0.4 | 1.26  | 0.59   | <0.3   | 1.0      | 2.5    | 17.6    |
| GGBFS| 32.7    | 13.0        | 0.3         | 43.0| 5.8 | -     | 0.4    | 1.4    | -        | -      | 0.7     | 15.3     |
| CG   | 72.43   | 1.24        | 0.43        | 13.43| 0.69 | 0.45  | 10.81  | 0.11   | -        | -      | 0.03    | 11.5     |

$^a$Loss on ignition.  
$^b$Median particle diameters (µm).

The activator was prepared by mixing 52% crushed glass and 48% NaOH solids by mass and adding a small amount of water. These mass ratios were selected to adjust the alkali-modulus of the activator by considering SiO$_2$ and Na$_2$O compositions of crushed glass and NaOH as 70% and 77.5% by mass, respectively. Next, the paste mixture was heated in a laboratory-grade oven at 150 °C for 2 hours based on the optimum conditions suggested by Vinai and Soutsos [9] and then the heated residue was ground down to a powder using mortar and pestle before use as the solid activator. The binder was prepared using 60% fly ash and 40% GGBFS by dry mixing with the solid activator first and then adding water. Alkali content of the binder (Na$_2$O%) was kept constant at 7.5% by considering the efficiency (EF%) of the activator with solid activator as 70% [10]. These results may be further described in detail in section 3.2. The effective water to binder ratio (W/B) was calculated by accounting for the crystalline water inside NaOH. Mix design parameters of both activator and binder are given in Table 2.
Table 2. Mix design details.

| Parameter              | Value |
|------------------------|-------|
| Na₂O%                  | 7.5   |
| AM                     | 1.0   |
| EF%                    | 70%   |
| Dry activator/Binder   | 0.21  |
| Effective W/B ratio    | 0.5   |
| FA                     | 60%   |
| GGBFS                  | 40%   |

The fresh ACB slurry was poured into cylindrical PVC moulds (38 mm x 76 mm cylinders with aspect ratio = 2.0) by three layers with 30 seconds of compacting by vibration on each layer. Casted samples were covered by a polythene wrap to avoid evaporating moisture in low humid environments. Then the covered samples were placed in a curing chamber with 20 °C and 95% relative humidity. After 1 day, samples were de-moulded, again sealed by a polythene wrap and placed in the same conditions for further curing until the required testing age of 1, 7 and 28 days.

2.2. Testing methods

Uniaxial compressive strength (UCS) tests were carried out using the Instron 50 kN compression frame with a 0.2 mm/min displacement rate. Three replicates were used for a particular test age, and all the samples were face-ground to make the compressive loading purely axial. X-ray diffraction (XRD) analysis was conducted for powder samples using Bruker D8 Cobalt diffractometer (Co Kα1-1.7889 Å radiation and 10–90° 2θ range) to identify the mineral phases of raw glass, solid activator, and hardened ACB paste after particular curing age. Semi-quantification analysis for the solid activator was conducted using DIFFRAC.EVA V4.3 software. FEI Quanta 3D scanning electron microscope (SEM) was used to visualize the morphology of the raw materials and reaction phases in the hardened ACB paste. Hardened paste samples were collected from the fracture surface after compressive testing, treated with acetone/ethanol to avoid further hydration and kept in the oven for 1h at 60°C before XRD or SEM analysis [11].

3. Results and discussion

3.1. Compressive strength

The strength properties of ACBs at different curing ages were investigated to find the effectiveness of the waste glass-based solid activator. Figure 1 shows the compressive strength development and corresponding Young’s modulus of the ACB paste up to 28 days of curing. At the early age of 1 day, ACBs showed lower values in strength and Young’s modulus. Furthermore, the early age cured samples showed more ductile behaviour than the brittle nature of 28 days cured samples. The 7 and 28 days strengths were around 17 and 30 MPa, which is acceptable to use as a binder in construction applications [12, 13]. The strength development with the curing age is also related to the improved microstructure described in section 3.3. According to the compressive strength results, glass-based solid activator ACBs showed comparable strengths over ACBs with commercial activators, such as NaOH and Na₂SiO₃.
3.2. Mineralogy

XRD tests were conducted on both solid activators to quantify the efficiency of forming Na$_2$SiO$_3$ and hardened ACBs to identify the mineral phases formed with the curing time. Figure 2(a) compares the nature of raw glass powder with the solid activator and shows a total amorphous nature of raw glass powder. Solid activator shows more crystalline nature with moreover flatted baseline compared to raw glass powder. According to semi-quantitative analysis, more than 70% of crystalline Na$_2$SiO$_3$ was formed by the total weight of phases. In addition, it shows minor crystalline phases of sodium carbonate (Na$_2$CO$_3$), different forms of sodium silicates (Na$_4$SiO$_4$, Na$_6$Si$_2$O$_7$) and calcium aluminium oxide (CaAl$_2$O$_4$). Hence, the efficiency of forming Na$_2$SiO$_3$ was assumed as 70% for mix design calculations of the ACB paste. Figure 2(b) shows the effect of curing age on the formation of mineral phases of hardened ACB paste. A noticeable increment in the crystalline peak can be observed for 28 days compared to 1-day ACB paste between the 2θ range of 32 and 37° which indicates the higher formation of calcium silicate hydrate (C-S-H) products in the binder phase [14]. This formation of C-S-H peaks also attributes to the strength increment with the curing age of ACBs described in section 3.1.

**Figure 1.** Variation of UCS and Young’s modulus of ACBs.
3.3. Microstructure
Surface morphology characteristics of raw glass powder and solid activator are shown in secondary electron images of Figures 3(a) and (b), respectively. The irregular particle morphology of the solid activator was affected by the odd shape of the raw glass particles. However, particles in solid activator show agglomerated nature which indicates a better reactive phase formed by micro-scale glass particles and NaOH micro-pearls due to the heat-treatment process. These micro-particles in the solid activator may dissolve in water and create basic media to leach out minerals of the solid precursors. Figures 3(c) and (d) show the backscattered electron images of hardened ACB paste at 1 day and 28 days curing age, respectively. After 28 days, the paste shows a dense structure with fewer unreacted phases than 1 day, which reduces the porosity and increases the strength characteristics.

4. Conclusions
This study elaborates the potential pathways to incorporate cementitious wastes in alkaline cement binders (ACBs) by involving fly ash, blast furnace slag, and crushed glass. Fly ash and blast furnace slag act as the solid precursors, while crushed glass behaves as the partial activator for the binder. Crushed glass powder can be successfully blended with commercial NaOH to produce a solid activator for one-part ACBs after thermal treatments. Glass powder-based activator showed 70% efficiency in creating crystalline sodium silicate, which is the major alkali-silica source for the activation of solid precursors. Moreover, the experimental results on strength, mineralogy, and microstructure of alkaline
cement paste show crushed glass substituted solid activator plays a similar role in one-part ACB systems compared to commercial activators. Finally, this study opens up the effective ways of recycling potential cementitious wastes, which produce a cement binder with better mechanical and microstructural properties.

![Figure 3. SEM images of (a) raw glass powder, (b) solid activator, (c) ACB paste – 1 day curing and (d) ACB paste – 28 days curing.](image)

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