Strength enhancement of alkaline activated fly ash cured at ambient temperature by delayed activation of substituted OPC

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HIGHLIGHTS

- OPC replacement shows 31% strength gain at 28 days compared to control sample.
- Strength enhancement was explained by delayed dissolution & activation of the OPC.
- Geopolymeric reaction is strongly influenced by OPC substitution.

ARTICLE INFO

ABSTRACT

Despite the considerable attention being paid to geopolymer concrete, its application has been limited due to its requirement of high temperature curing. In this study, we aim to increase the reactivity of fly ash at ambient condition by substituting OPC in high-alkaline medium. A series of experiments of compressive strength test, heat flow measurement, XRF, XRD, and SEM analysis is conducted to understand the mineralogical and microstructural impacts of the substituted OPC. The XRD experiments reveal that abundant Ca source in fly ash and OPC transforms to katoite and amorphous phases of C-A-S-H and C-S-H. The formation of zeolite precursors was also influenced by the OPC substitution. Furthermore, the delayed dissolution and activation of OPC in high-alkaline medium that observed by reaction heat measurement, play a positive role of filling existing voids which can efficiently enhance mechanical strength of complex system.

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1. Introduction

Ordinary Portland Cement (OPC) is one of the most widely used manufactured materials around the world. During its manufacturing process, unavoidable high temperature firing and direct CO_2 emission cause significant environmental problems. It contributes to approximately 5% of global CO_2 emissions [1,2]. Cement and concrete industries have therefore been searching for more sustainable alternatives.

Geopolymer is an emerging alternative binder to OPC. It is an inorganic polymer which is synthesized by activating aluminosilicate materials with alkaline solutions. The raw materials can be industrial by-products (e.g. fly ash and blast furnace slag) or natural minerals (e.g. natural pozzolan, metakaolin, and calcined clay) [3–7]. Since it can be produced by utilizing solely industrial by-product materials or natural minerals without high temperature

firing, its manufacturing process produces low CO_2 emission in comparison to that of OPC. It has therefore been actively researched in both academia and industry, and the mechanism of the alkali activation process has been rigorously studied over the last few decades [7,8].

For geopolymer concrete, the types of starting aluminosilicate powder and the activator solutions determine the reaction mechanism and the final reaction products [7]. The main reaction product in geopolymers is an aluminosilicate gel, in which tetrahedral sites are charge-balanced by alkali cations. The most widely used activators are alkali silicates, hydroxides, or a combination of these chemicals. It has also been suggested that the reactivity of aluminosilicate materials in alkali solutions is highly dependent on reactive silica, alumina, and amorphous phase content in raw materials [9]. In addition, the calcium compound in the source material plays a vital role since Ca ion is capable of acting as a charge-balancing cation within the geopolymeric binder [10]. Furthermore, the available Ca ions in slag or OPC enable the coexistence of geopolymeric gel and Calcium-Silicate-Hydrates (C-S-H) that has been

found to increase the mechanical strength of geopolymer materials [5,11].

Despite the significantly reduced environmental impact of geopolymer concrete, it has not been well adapted in the construction industry. The main reason is a high temperature curing requirement. Typically, fly ash based geopolymer pastes harden slowly at ambient temperature and have low ultimate strength [7]. Hence, it is usually subjected to heat curing at temperatures ranging from 50 to 80 °C, which is only viable for precast concrete production. Therefore, it is critical to develop a geopolymer concrete that can be cured in ambient condition in order to increase the use of geopolymer concrete in normal cast-in-situ concrete applications. This can significantly decrease the carbon footprint generated from the construction industry. To address this problem, a number of studies have been conducted to enhance the reactivity of fly ash in an alkaline environment by incorporating additives such as silica fume, metakaolin, or OPC [12].

In order to use OPC as an additive for fly ash based geopolymer, the hydration mechanism of OPC in a highly alkaline medium should be understood. While the hydration of OPC in water has been extensively studied [13], only a few researchers have studied OPC hydration in high-alkaline solution. It was revealed that the hydration of cement is retarded by the presence of alkaline concentration [8]. When fly ash is partially replaced with OPC, the composite has the highest compressive strength with a combination of water glass (sodium silicate) and NaOH [14]. Wang et al. investigated the effect of NaOH addition on the compressive strength of fly ash pastes with cement kiln dust [15]. In addition, Tailby and MacKenzie compared the mechanical strength of geopolymer, OPC, and various fly ash composites substituted with cement minerals. They found lower strength when mixing with synthetic cement minerals compared to OPC [16]. In general, the addition of calcium oxide is believed to form additional C-S-H, a main binding product in concrete, along with aluminosilicate gel under high-alkaline concentration [14]. Overall, the hydration of OPC in highly alkaline solutions alters its hydration process, with considerable delays in the formation of the main reaction products [8,17].

To increase the reactivity of fly ash for geopolymerization at ambient curing condition, OPC is used in this study as a substitute to supply additional calcium ions. This approach requires the knowledge of OPC hydration in high alkaline solution and fly ash-based geopolymerization at ambient condition, as well as an interaction chemistry between calcium silicate and aluminosilicate systems. However, research on the hydration products of geopolymer cured at ambient condition is scarce in the literature due to its low strength evolution. Recently, Oh et al. widely investigated the mechanical strength obtained by using different fly ashes at different curing conditions [18]. At ambient condition, most of the alkali-activated fly ashes did not have suitable strength as construction materials. On the other hand, some researchers have examined similar methods by anticipating the beneficial effect of the exothermal heat generated from the reaction of OPC and water. The compressive strength achieved of geopolymer concrete with OPC additive ranged from 45 to 68 MPa with a solid/binder (s/b) ratio of 0.4 [19,20]. In addition, by controlling the fineness of fly ash, the reactivity increased and thus enhanced the mechanical properties of the combined mortars [20].

Considering the variability and intrinsic complexity of fly ash and the complicated reaction of the two-component system, understanding the hybrid reactions of both fly ash and OPC in alkaline solution is challenging. Thus, it is not surprising that some researchers reported good results, while others did not. In this study, we aim to clarify the reaction process of geopolymer with OPC additive, especially for pastes cured at ambient condition. A series of experiments using reaction heat measurement, a strength test, X-ray diffraction, and microscopic analysis were conducted.

2. Experimental details

Elemental compositions of used fly ash and cement are presented in Table 1. Fly ash type C was supplied by Headwaters Resources, Inc. (Fig. 1). The particle size distributions of fly ash and cement are shown in Fig. 2. To investigate the reaction products and engineering properties, samples were prepared with s/b ratios of 0.6 and 0.8. For each s/b ratio, OPC was substituted with fly ash as 10%, 20%, and 30% of the total binder weight. As alkaline solution, NaOH (10 M) and sodium silicate (Ms = 3.22) were used, as determined from the previous studies on geopolymer and alkali-activated OPC [3,5,14]. Table 2 shows the mix design proportions. Fly ash was uniformly mixed with the designed amount of OPC for 5 min then mixed with alkaline solution for 2 min. The samples were then cast in cylindrical molds of φ 2.54 cm × 2.54 cm and covered with plastic wrap. The samples were stored in an environmental chamber (25 °C, 95% RH) until testing.

The chemical compositions of the OPC and fly ash were analyzed by X-ray Fluorescence (XRF) (Rigaku NEX CG) on a pressed pellet after homogenizing the material for 5 min in a mill. A total measurement time of 20 min was selected to obtain a reliable signal. The measured oxide composition is shown in Table 1.

X-ray Diffraction (XRD) analysis was performed for raw materials (OPC and fly ash) and activated samples at 28 d of curing. At 28 d of curing, the activated samples were finely ground and tested without further processes. In addition, the internal standard method for the quantification of amorphous material was only used for raw materials. 10 wt.% of ZnO (NIST SRM 674b) was uniformly mixed with each raw material before the XRD measurement. A Cu X-ray source with 40 kV was used to cover a 2theta range from 3° to 80° with a step size of 0.0033° (Rigaku Miniflex). Rietveld analysis was applied for the clinker using Highscore Plus software [21]. The crystalline phases were identified by subtracting the background and comparing the peak positions and intensities with those of the Inorganic Crystal Structure Database (ICSD). The scale factors, the peak shape parameters of W, V, and U, and the asymmetry, preferred orientation, and unit cell parameters were subsequently refined. Fig. 3 shows the fitted patterns for the OPC and fly ash with a goodness of fit value of 5.8 and 9.6, respectively. Accordingly, the quantitative results of Rietveld analysis are presented in Tables 3 and 4. In the cases of activated samples, only qualitative comparisons were made due to the mineralogical complexity induced from the amorphous phases in raw materials and the low degree of crystallinity of two reaction products (i.e., C-S-H and aluminosilicate gel).

Compressive strength was measured at 1, 3, 7, 14, and 28 d of activation. The compressive strength tests on three replicates from each mix design were performed using a Shimadzu universal testing machine. The averaged results with standard deviation error bars are summarized in Table 5 and Fig. 4.

An isothermal calorimeter (TAM Air) was used to measure the rate of activation heat for the first 72 h. For all samples, 15 g of mixed paste was placed into a glass vial. The sealed vials were placed into the calorimeter and the heat flows were simultaneously measured for 72 h. The total heat of hydration was determined from the integration of the heat flow curve between 30 min and 72 h. For both heat flow and total heat of hydration, the obtained data were normalized by the weight of the binder as shown in Fig. 5.

Two samples (FA1_0.6 and FA0.7_0.6) were selected for Scanning Electron Microscopy (SEM) analysis. The samples were epoxy-impregnated and polished before carbon-coating for the analysis. Back Scattered Electron (BSE) images and multiple Energy-Dispersive Spectroscopy (EDS) spectra were obtained using a Field-Emission-SEM (FE-SEM, JEOL JSM-7800F) with an accelerating voltage of 15 kV.

3. Raw materials characterization

As starting source materials, the mineralogical compositions of fly ash and OPC are critical to understand the reaction chemistry of the proposed complex system. However, the characterization of raw materials has not always been rigorously performed in previous studies on fly ash-OPC alkali-activated [19,22]. It includes missing mineralogical information on raw materials. Herein, the used fly ash contains 23.4 wt.% of CaO component (Table 2). As introduced in the previous section, this abundant Ca source can play a positive role of strength enhancement in an alkaline environment [14]. The SEM study indicates that the fly ash particles are mainly fine spheres (Fig. 1), of which the size ranges from 1 to 100 μm. Compared to that of OPC, it has a wider range of particle sizes (Fig. 2).

Similar to our previous research [23], quantitative X-ray diffraction analysis was performed on raw materials with the addition of zinc oxide (10 wt.%). The major crystal phases identified in fly ash include quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), and periclase (MgO). Also, the presence of the glassy phase is illustrated by a hump in the range of 20–40° (Fig. 3) and calculated as 85 wt.%. Since the