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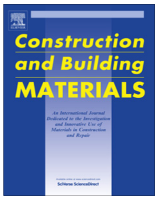

Effects of addition of $Al(OH)_3$ on the strength of alkaline activated ground blast furnace slag-ultrafine palm oil fuel ash (AAGU) based binder

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HIGHLIGHTS

- This study investigated the effects of $Al(OH)_3$ on the alkaline-activated-binder.
- The possibility of formation of different distinctive products is established.
- $Al(OH)_3$ enhances Si–Al substitution, amorphousity and carbonation of the products.
- The 3-day compressive-strength of 42–49.5 MPa with inclusion of 3–4 wt.% $Al(OH)_3$.

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ABSTRACT

Effects of $Al(OH)_3$ content on the compressive-strength of alkaline activated ground blast furnace slag (GBFS)-ultrafine palm oil fuel ash (UPOFA) based mortar (AAGU) were investigated. The mortar was activated with combined activators (Na_2SiO_{3aq} of silica modulus ($Ms = SiO_2/Na_2O$) of 3.3 and 10 M $NaOH_{aq}$). The Scanning Electron Microscope couple with energy dispersive X-ray (SEM + EDX) revealed the possibility of formation of distinctive products of calcium-silicate-hydrate (C-S-H) and Ca/Na-alumino-silicate-hydrate (C/N-A-S-H) while Fourier transform infra-red spectroscopy (FTIR) revealed the existence of higher degree of Si–Al substitution, amorphousity and carbonation as a result of inclusion of $Al(OH)_3$ in the mixture. The 3-day compressive-strength of $AAGU_{Al}$ mortar increased with $Al(OH)_3$ up to optimum value of 4 wt.% of PMs (GBFS + UPOFA) but started decreasing when the $Al(OH)_3$ is outside the optimum. The strength of 42–49.5 MPa could be achieved at the $Al(OH)_3$ dosage of 3–4 wt.% while the equivalent SiO_2/Al_2O_3 molar-ratio ranged from 6.72 to 8.94.

1. Introduction

Alkaline activated binder is the process of activating prime materials that contained high Si + Al or Ca + Si system using different alkaline activators of hydroxyl or silicate of alkaline metals to form two group products of $Me_2O–MeO–Me_2O_3–SiO_2–H_2O$ and $Me_2O–Me_2O_3–SiO_2–H_2O$ identified with geopolymer and alkaline activated slag (AAS) system, respectively [1]. However, there are some solid waste materials that contained very higher Si and Ca but lower content of Al. It is expected that augmenting the alumina components of those materials may not only bring a safe environmental condition but also better the valorization of these wastes. A typical example is palm oil fuel ash (POFA) which have been identified to be pozzolanic [2–4]. There is proliferation of these materials in Malaysia and Thailand, so much that about 0.1 million ton of POFA is generated annually in Thailand while 3 million tons of POFA was produced in Malaysia in the year 2007 [5]. In another vein, blast furnace slag contained high Ca and its performance as a good prime materials for AAS have been established [6–9].

Second, high Ca^{2+} has been reported to contribute to the stability of aluminosilicate formation or contribute to the formation of additional products of Ca-aluminosilicate-hydrate existing simultaneously with calcium silicate hydrate (C-S-H) [10–13]. Therefore, addition of Al is expected to improve the performance of the product and reduce the resulting Ca/Al or Si/Al ratio that are required for optimum strength performance. In the light of this, Chindaprasirt et al. [14] have studied effects of Si and Al incorporation in high Ca-based fly-ash geopolymer system. They reported that additions

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of these mineral elements shorten the setting time due to formation of calcium-silicate-hydrate (CSH) and calcium-alumino-silicate-hydrate (CASH).

Garcia-Lodeiro et al. [15] observed that Al at high pH modified C-S-H structure, thereby increasing the degree of polymerization in (alumino) silicate on one hand and also established that the optimum range of Si/Al ratio between 3.20 and 3.70 favored longest setting time with highest strength. De Silva and Sagoe-Crenstil [16] has reported that low SiO_2/Al_2O_3 or high content of Al_2O_3 led to product low strength in metakaolin (Na–Al–Si) based geopolymer system and found the optimum range of SiO_2/Al_2O_3 to be 3.4–3.8 and posited that the inclusion of Al_2O_3 also affected the amorphousness of the system. In the contrary, SiO_2/Al_2O_3 molar ratios lower or higher than 3.8 in conjunction with increase in the Na_2O content tends to favor amorphous–crystalline transformation [17].

Therefore, in order to improve the strength achieved in an alkaline activated binder developed by utilizing these high-calcium GBFS and high-silica ultrafine POFA (UPOFA) as base materials, there is need to study the effects of incorporation of inorganic alumina compounds such as $Al(OH)_3$ on the resulting products. These resulted in the accompanied change in SiO_2/Al_2O_3, H_2O/Na_2O, Ca/Si ratios and the compressive strength of the product. This study will also help us to understand the roles played by inorganic Al source on the microstructural modification of the product, and better facilitate understanding the chemistry of the alkaline activated GBFS–UPOFA based mortar.

2. Materials and methods

2.1. Materials

2.1.1. Ultrafine palm fuel ash (UPOFA) and ground blast furnace slag (GBFS)

Palm oil fuel ash (POFA) and blast furnace slag (BFS) were collected at Malaysian Southern Steel Company and United Palm Oil Industry, respectively. These two raw materials were first heated at 105 °C ± 5 °C for 24 h to remove the inherent moistures after which it was sieved through 300 μm size sieve. The BFS was later ground for 16 h to obtain the ground BFS (GBFS) while POFA was first ground for 8 h and calcined at 500 °C ± 50 °C in the gas powered furnace for 90 min. It was then subsequently milled for additional 8 h to obtain ultrafine POFA (UPOFA). The milling was done with mechanical rotating drum at the speed of 180 rpm. The drum contained 150 balls of different sizes ranging from 6 mm to 32 mm.

Turbotrac instrument model *S360* particle size analyzer (PSA) and *Micrometrics ASAP2020* BET equipment using nitrogen gas adsorption were used for determining the particle size distributions (PSDs) and surface areas (SAs), respectively. The oxide compositions of the pozzolanic materials (PMs)–GBFS and UPOFA-were determined using X-ray florescence (XRF) technique.

2.1.2. Alkaline activators and aluminum hydroxide $Al(OH)_3$

The combined alkaline activators (CAA) comprised commercially available Na_2SiO_{3aq} of initial silica modulus ($Ms = SiO_2/Na_2O$) of 3.3 and 10 M $NaOH_{aq}$. The percentage compositions of Na_2SiO_{3aq} are as follows: H_2O: 62.11 wt.%, SiO_2: 29.13 wt.% and Na_2O: 8.76 wt.%. The distilled water and NaOH pellets of 99% assay (purity) was used to prepare 10 M $NaOH_{aq}$ with 404.04 g of the pellets being dissolved in 1 L of solution. The total silica modulus of CAA ($Ms = SiO_2/Na_2O$) is expressed as shown in Eq. (1). The commercially available white powder $Al(OH)_3$ with CAS No: 21645-51-2 was also used as a source of Al. The $Al(OH)_3$ is composed of Al_2O_3: 65.38 wt.% and H_2O: 34.62 wt.% as shown in Eq. (2) below:

$$Na_2O \cdot nSiO_{2aq} \rightarrow Na_2O + nSiO_2 + H_2O \tag{1}$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \tag{2}$$

2.1.3. Aggregates

Total aggregates (TA) comprised 100% dune sand as fine aggregate (FA) of fineness modulus of 1.85. The FA/PM ratio was 1.8 and the specific gravity of FA in the saturated surface dry (SSD) conditions was 2.62.

2.2. Experimental design

2.2.1. Mixture proportion for alkaline activated GBFS–UPOFA (AAGU) mortar

The AAGU mortar was prepared at the constant GBFS/PMs, Na_2SiO_{3aq}/10 M $NaOH_{aq}$, CAAs/PMs, free water content (FWC), that is, FWC/PMs and FA/PMs mass ratios of 0.2, 2.5, 0.5, 0.02 and 1.8, respectively. The mortar mix proportion was based on the unit weight of 2400 kg/m^3 as shown in Table 1. The $Al(OH)_3$ powder content which varied as 2, 3, 4, 5 and 6 wt.% was added to the AAGU mortar mixtures to become $AAGU_{Al}$.

2.2.2. Mixing, placement and testing of AAGU mortar

The raw materials were mixed in planetary bench mixer of 4.73 L capacity. The PMs were first mixed for 2 min to remove the air pockets. This was then followed with addition of FWC, 10 M $NaOH_{aq}$, Na_2SiO_{3aq}, and FA such that the total mixing time was 10 min. The mortars were cast in two layers in an oil smeared steel mould of dimension 50 × 50 × 50 mm. Each layer was vibrated for 15 s. The samples were then preserved in the laboratory by covering it with vinyl bags to prevent moisture loss at temperature of 25 °C for 12 h after which, was demoulded.

The demoulded specimens cured in an oven at 60 °C for 24 h were wrapped with heat resistant vinyl sheet [18,19]. The cured samples were kept again in the laboratory at 25 °C until ready for 3-day compressive-strength testing; having realized through separate study that more than 80% of the maximum strength of heat-cured AAGU binder was obtained in 3 days. The compressive strength test was done using the universal crushing test machine at the loading rate of 0.9 kN/s. The average failure load per cross sectional areas (MPa) of the three specimens was then recorded.

2.3. Analytical methods

The *JEOL* scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM + EDX) model *5800 LV*, was used to observe the morphology of the fractured 14 days solid of $AAGU_{Al}$ and AAGU samples cured at 60 °C and in the duration of 24 h. EDX was performed at an accelerating voltage of 15 kV. The pulverized dry paste samples were used for the Fourier transform infrared (FTIR) spectroscopy to identify the bonds and functional group that existed within the binder matrices. The FTIR spectroscopy was done using *Perking Elmer 880 spectrometer* (KBr pellet technique) while XRD testing of the original samples were determined using *Rigaku* instrument model *Ultima IV* scanning from 0 to 80, 2θ. The $AAGU_{Al}$ ($Al(OH)_3$-4%) were used for SEM + EDX and FTIR to study the effects of Al in the AAGU mortar while AAGU ($Al(OH)_3$-0%) prepared with the same material composition was used as the control.

3. Results and discussion

3.1. Physical properties of the pozzolanic base materials (PMs)

From Table 2, UPOFA has a higher percentage composition of SiO_2, Fe_2O_3, K_2O, and P_2O_5 than GBFS while GBFS in turn, contained higher composition of MgO, CaO, and SO_3 than UPOFA. The former also has the composition of Na_2O, TiO_2, K_2O, and P_2O_5 of less than 1% each while the latter has only TiO_2 and Na_2O in the trace amount. GBFS and UPOFA have Al_2O_3 of approximately 4% compositions. The GBFS basicity coefficient ($k_b = CaO + MgO/SiO_2 + Al_2O_3$) and quality coefficient ($Q_c = CaO + MgO + Al_2O_3/SiO_2 + TiO_2$) were 2.10 and 2.59, respectively. Hence, it is regarded as basic slag ($K_b > 1$) [8,20].

The particle sizes of the GBFS and UPOFA that were less than 1.1 μm contributed immensely to their reactivities. It has been reported that GBFS sizes below 2 μm react completely within approximately 24 h in blended cements and alkali-activated systems [21,22]. The grinding of these base materials to achieve the surface area of more than 13 m^2/g as shown in Table 3 also contributed to their reaction kinetics that increased due to finely divided nature of the materials thereby increased the compressive strength of the mortar [23].

Fig. 1 shows XRD diffractogram of the original GBFS and UPOFA. The peaks in UPOFA include calcite ($CaCO_3$), cristobalite (SiO_2), quartz (SiO_2) and potassium aluminate phosphate ($k_2Al_2(PO_4)_3$). The peaks in GBFS consist of wollastonite ($CaOSiO_2$), gehlenite ($CaOAl_2O_3SiO_2$) and akermanite ($CaOMgOSiO_2$). The broader nature of GBFS diffractive halo that centered on 33.9° suggests that it is