Journal of Advanced Concrete Technology

Materials, Structures and Environment

Performance of Different Grades of Palm Oil Fuel Ash with Ground Slag as Base Materials in the Synthesis of Alkaline Activated Mortar

Moruf. O.Yusuf , Megat A. Megat Johari, Zainal A. Ahmad, Mohammed Maslehuddin

Journal of Advanced Concrete Technology, volume 12 (2014), pp. 378-387

Related Papers [Click to Download full PDF!](#)

Flexural Behaviour of Reinforced Lightweight Concrete Beams Made with Oil Palm Shell (OPS)

Md. Abdul Mannan, Delsye C. L .Teo, John V. Kuriam

Journal of Advanced Concrete Technology, volume 4 (2006), pp. 459-468

Mechanical Properties and Durability of Normal and Water Reduced High Strength Grade 60 Concrete Containing Rice Husk Ash

Hilmi B. Mahmud, Muhammad A. Abdul Malik, Rahaimi A. Kahar, Muhammad A. Zaini

Journal of Advanced Concrete Technology, volume 7 (2009), pp. 21-30

Improving the Engineering and Fluid Transport Properties of Ultra-High Strength Concrete Utilizing Ultrafine Palm Oil Fuel Ash

Ahmad N. Mohammed , Megat A. Megat Johari , Abdullah M. Zeyad, Bassam A. Tayeh

Journal of Advanced Concrete Technology, volume 12 (2014), pp. 127-137

[Click to Submit your Papers](#)

Japan Concrete Institute <http://www.j-act.org>

Technical report

Performance of Different Grades of Palm Oil Fuel Ash with Ground Slag as Base Materials in the Synthesis of Alkaline Activated Mortar

Moruf Olalekan Yusuf^{1,3}, Megat Azmi Megat Johari^{1*}, Zainal Arifin Ahmad² and Mohammed Maslehuddin³

Received 25 April 2014, accepted 28 September 2014

doi:10.3151/jact.12.378

Abstract

This study examined the alkaline activated ground slag (GS) blended with different grades of palm oil fuel ash (POFA), namely: ground POFA (GPOFA), treated or calcined GPOFA (TPOFA) and ground TPOFA or ultrafine POFA (UPOFA) in the synthesis of alkaline activated GS-POFA mortar (AAG-POFA). The AAG-POFA mortars were prepared with 8M- NaOH_{aq} and $\text{Na}_2\text{SiO}_{3\text{aq}}$ ($M_s = \text{SiO}_2/\text{Na}_2\text{O} = 3.3$) activators, and then cured at 60 °C for 24 h. The findings showed that the grinding and calcination of POFA reduced the carbon content, loss on ignition, enhanced its fineness and increased the mineral (oxide) compositions. The grades of POFA used for the synthesis of AAG-POFA products impacted the morphologies of its microstructures, compressive strength, carbonation and amorphousity. TPOFA and UPOFA could be successfully used for the synthesis of AAG-POFA mortar with considerable structural strength. While AAG-UPOFA produced the highest mortar strength, the production of AAG-TPOFA mortar was more energy conservative. Finally, GPOFA was practically unsuitable for the synthesis of AAG-POFA as it resulted in low strength products while its mixture was characterized with low consistency, and poor dissolution or hydroxylation upon reacting with the alkaline activators.

1. Introduction

Finding an alternative binder to ordinary Portland cement (OPC) has become necessary due to the proliferation of CO_2 that accompanies the breaking down of limestones during its manufacturing process (Davidovits 1999; Pacheco-Torgal *et al.* 2008). As a result of this, OPC annual consumption is reported to contribute about 5-7% of global atmospheric and anthropogenic CO_2 emission (Huntzinger and Eatmon 2009; Meyer 2009). Therefore, there is need to cut short the consumption of OPC by reducing its utilization in the construction industry. Some of the identified pozzolanic materials that have been used as supplementary cementitious materials (SCMs) in mortar and concrete production with a view to reducing OPC utilization include industrial and agro-solid wastes such as slag and palm oil fuel ash, respectively.

Palm oil fuel ash (POFA) is produced in large quantities such that about 70% of the raw materials used in the palm oil production results in solid wastes (Chandara *et al.* 2010). POFA solid wastes include fibers, nutshells,

and empty fruit bunches. These solid wastes were burnt to provide heat energy needed by the boiler to produce required steam needed for the generation of electricity in the biomass thermal plants (Karim *et al.* 2011). Significant amount of the resulting ashes, known as palm oil fuel ash (POFA) was generated; about 3 million tons was produced in Malaysia in 2007, while about 0.1 million tons of POFA was produced annually in Thailand (Chindaprasirt *et al.* 2007; MPOB 2013). Increase in organic impurities, carbon content, and low fineness of POFA sizes have limited its utilization as a SCM in concrete and mortar production (Budiea *et al.* 2010; Chandara *et al.* 2010; Megat Johari *et al.* 2012). Ground slag (GS) on the other hand, is a waste material that is obtained in the production of iron or steel. It has low reactivity in water but highly reactive in alkaline medium (Manso *et al.* 2005; Shi 2002), especially if it is dominated by Ca+Si phase (Li *et al.* 2010).

Many researchers have tried to utilize POFA as SCMs in concrete production but in limited quantities. For instance, Tay (1990) reported that not more than 10% of POFA could be used as a partial SCM in concrete production simply because of its high carbon contents, and larger particle sizes, which culminated against its pozzolanic reactivity. Budiea *et al.* (2010) also maintained that inclusion of up to 20% POFA of average size of 10 μm performed better than coarser particle sizes (45 μm) in the production of OPC concrete designed to resist hydrochloric acid (HCl) attack. Kroehong *et al.* (2011a) also studied POFA-OPC pastes and reported that 30% POFA-OPC replacement in concrete resulted in the maximum compressive strength as a result of good aggregate-binder packing effects. Hussin and Abdul Awal

¹School of Civil Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia.

*Corresponding author,

E-mail: cemamj@usm.my; moruff@gmail.com

²Structural Materials Niche Area, School of Materials and Mineral Resources, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia.

³Center for Engineering Research, Research Institute, King Fahd University of Petroleum and Minerals, 31261 Dhahran, Saudi Arabia.

(1998) also asserted that 30% of POFA-OPC replacement in the concrete subjected to wetting and drying cycles samples showed a good resistance to sulfate attack (10% Na₂SO₄).

Further treatment of POFA had been reported to cause an improvement in its physical and chemical properties. To this end, Megat Johari *et al.* (2012) have reported that de-carbonization of POFA by subjecting it to heating (calcination) and milling improved its reactivities in OPC-POFA concrete. Carbon content and fineness are two differentiating factors in the three identified grades of POFA namely: *ground POFA* (GPOFA), *treated or calcined GPOFA* (TPOFA) and *ultrafine or ground TPOFA* (UPOFA). Besides, carbon contents and fineness of POFA have significant impacts not only on the strength but also on the microstructure of the products. In fact, about 60% of UPOFA has been successfully used as SCMs in OPC-POFA blended concrete (Megat Johari *et al.*, 2012) because of its enhanced pozzolanic reactivity and pore filling capability (Jaturapitakkul *et al.* 2011; Kroehong *et al.* 2011b; Megat Johari *et al.* 2011).

Despite these studies on POFA as pozzolanic materials in mortar and concrete production, there are still gaps in the understanding of the performance of GPOFA, TPOFA and UPOFA - as base materials in the synthesis of alkaline activated GS-POFA mortar (AAG-POFA) on one hand and the examination of performance of the synergy of slag and POFA in terms of strength and microstructure of AAG-POFA on the other. Therefore, this study aims at understanding the microstructural effect and strength of different grades of POFA in combination with ground slag in the synthesis of alkaline activated mortars, which were designated AAG-GPOFA, AAG-TPOFA and AAG-UPOFA. Finally, apart from the underlined objective of this study as previously stated, it also fosters the understanding of the microstructures and characterizations of the resulting AAG-POFA mortars.

In the long run, this study will contribute to the environmental sustainability, efficient use of energy in the material preparation and fosters the provision of alternative “green” binder to OPC-based products, especially for construction and other civil engineering applications.

2. Materials and methods

2.1 Materials

2.1.1 Palm oil fuel ash of different grades and slag

Slag (S) and palm oil fuel ash (POFA) were obtained from Malaysian Southern Steel Company and United Palm Oil Industry, respectively. These pozzolanic materials (PMs) were heated in the oven at 105 °C ± 5 °C for 24 h to remove their inherent moistures. This treatment was followed by screening the materials through 300

microns sieve (ASTM: E-11 #50). Thereafter, POFA was ground for 8 h to obtain fine ground *POFA* (GPOFA) by using electric powered and mechanical driven ball-milling drum machine, rotating at 180 rev/min. The machine contained 150 pieces of ball bearings of varying diameters that ranged from 6 mm to 32 mm.

The GPOFA was further ground to become finer and

POFA → Ground POFA → Treated POFA → Ultrafine POFA

Heat at 105 °C
Ground for 8 h

calcined at 500 °C
for 90 mins

Ground for 8 h

later heat-treated at 550 °C ± 50 °C for 90 mins to produce *treated or calcined GPOFA* (TPOFA), which was in turn re-milled for additional 8 h to obtain ground TPOFA or *ultrafine POFA* (UPOFA). Similarly, slag was ground for 16 h to obtain ground slag (GS).

Microtrac (*Turbotrac*) instrument model S3500 particle size analyzer (PSA) was used to determine the materials particle size distributions (PSDs) while *Micromeritics ASAP2020* equipment, which used nitrogen gas adsorption was utilized in the determination of BET surface areas of PMs (GS and POFA). The oxide compositions were determined using x-ray fluorescence (XRF) technique.

2.1.2 Preparation of alkaline activators

The alkaline activators used were commercially available Na₂SiO_{3aq} (NS) with initial silica modulus (Ms = SiO₂/Na₂O) of 3.3 together with 8M NaOH_{aq} (NH). The Na₂SiO_{3aq} had the initial compositions of H₂O: 62.11%, SiO₂: 29.13% and Na₂O: 8.76%. The solution of 8M NaOH_{aq} was obtained by dissolving 323.33 g of NaOH_{aq} pellet (purity - 99% assay) in distilled water to make 1 liter of 8M-NaOH_{aq} solution (NH). The total weight of activators was the sum of NS and NH (CAA = NS + NH), which was expressed as the ratio of pozzolanic materials (PMs).

2.1.3 Aggregates

The mortar specimens were produced using the fine dune sand or fine aggregate (FA) with fineness modulus of 1.85, and the specific gravity of 2.62 measured in the saturated and surface dry (SSD) conditions.

2.2 Experimental design

2.2.1 Mixture proportions

The alkaline activated GS-POFA mortar had an approximate unit weight of 2200-2400 kg/m³. The prepared mortars were composed of GS/PMs, CAA/PMs, NS/NH and FA/PMs mass ratios of 0.2, 0.5, 2.5 and 2.75, respectively as shown in **Table 1**. Free added wa-

Table 1 Composition of alkaline activated of ground slag and palm oil fuel ash.

Mixture	xPOFA kg/m ³	GSS kg/m ³	Sand kg/m ³	Water kg/m ³	Na ₂ SiO _{3aq} (MS = 3.3)	8M NaOH _{aq} kg/m ³	unit weight
AAG-POFA	412.2	103.0	1416.9	10.3	184.0	73.6	2200.0

AAG-POFA means alkaline activated ground slag and palm oil fuel ash (of different grades) mortars

ter content (FWC) expressed as a percentage of PMs (FWC/PMs) of 2wt.% was added to all the mixtures.

2.2.2 Mixing, placement and testing of AAG-POFA mortar

The constituent materials were mixed in 4.7 L capacity planetary bench mixer. The PMs were first mixed for 2 mins to remove the air pockets. This was followed by adding free water content (FWC), 8M NaOH_{aq} (NH), Na₂SiO_{3aq} (NS), and sand (FA), such that the total mixing time was 12 mins. The mixture cast into oil smeared steel mould of dimension 50X50X50 mm³, tamped, compacted and vibrated in two-layer for 15 secs each. Prior to casting, the flow of each mix was determined in accordance with (ASTM: C-1437, 2013).

Subsequently, the cast samples were covered with polythene sheet to prevent moisture loss and then preserved for 12 h (delay periods) in the laboratory (25 °C) to allow them to be strong enough for demoulding. The demoulded samples were then kept in the heat-resistant vinyl bag "Diamond" before being cured at 60 °C for 24 h. The choice of the activated temperature and the curing duration have been established to be favourable to the strength development in a separate study (Yusuf *et al.*, 2014b). The 3, 14 and 28-day compressive strength test were determined using the compressive strength testing machine at the loading rate of 0.9 kN/s while the average loads of three (3) specimens for each mixture divided by the cross-sectional areas was recorded as the resulting compressive strength (MPa).

2.3 Analytical methods

Field emission scanning electron microscopy coupled with energy dispersive x-ray analysis (FESEM + EDS) of the products were done with ZEISS SUPRATM + EDAX Genesis model 35 VP to observe the morphology and elemental composition of the mortars, respectively. The EDS was performed at an accelerating voltage of 15 kV. The pulverized dry activated mortar specimens were used for the Fourier transform infrared (FTIR) spectroscopy by using Perking Elmer 880 spectrometer (KBr pellet technique). X-ray diffraction analysis (XRD) was done using the semi-quantitative X-ray diffraction (XRD) analysis by using Bruker D8 Advance of CuK_α monochromatic radiation ($\lambda = 1.5406 \text{ \AA}$), 2θ from 10° to 90°; with step interval 0.0341° and step time 71.6 scanning from 0 to 80 (2θ) while PANalytical X'Pert Highscore Plus software was used for the XRD analyses.

X-ray florescence analyses (XRF) was obtained by using XRF-spectrometer model Rigaku RIX 3000 with a fully automated programmable operation of Rh/W

dual X-ray tube, which is capable of analysing liquid, solids and powder. The instrument is also capable of conducting semi-qualitative analysis of the chemical compositions by fusing or pressing the sample at high temperature to ensure uniformly dispersed solid solution. This method also prevented the effects of powder grain sizes and mineralogical interactions. The on-board computer was capable of reducing the data in terms of elements or oxides of the elements present in the samples (metallic and non-metallic). The results are as shown in Table 2. There had been good correlation between the oxides and the elemental compositions of the adopted semi-quantitative analysis (Warren and Shadforth 1999).

3. Results and discussions

3.1 Physical properties of the pozzolanic base materials (PMs)

XRF results in Table 2 shows carbon content (C), loss on ignition (LOI) and oxides compositions of GS and POFA. From XRD diffractogram in Fig. 1, GS shows

Fig.1 XRD diffractogram of raw palm oil fuel ash and ground slag.

Table 2 Oxide percentage compositions of ground slag and different grades of palm oil fuel ash.

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	TiO ₂	MgO	K ₂ O	P ₂ O ₅	SO ₃	C	LOI
GPOFA	46.00	3.10	2.45	8.46	0.13	0.13	4.40	4.08	3.95	0.30	26.44	21.60
TPOFA	59.67	4.22	3.39	10.67	0.19	0.19	5.66	5.25	4.94	0.45	4.88	2.57
UPOFA	60.42	4.26	3.34	11.00	0.18	0.19	5.31	5.03	4.48	0.45	4.86	2.55
GS	25.78	4.42	1.94	53.54	0.03	0.26	9.50	0.05	0.04	3.85	0	2.05

better amorphousness by wider diffractive halo between 20-40° (2-theta angle). Within these 2-theta angles, the curvature of GS was quite conspicuous compared to POFA powder, which shows a less curvature or concavity at the same range. The amorphousness of GS could be as a result of the presence of short-range order of Fe₂O₃-SiO₂-Al₂O₃-CaO-MgO- in its network (Antipas *et al.*, 2012). The presence of less percentage of MgO and CaO in POFA compared to GS as reflected in **Table 2** also supported this assertion. This was why there was a more diffractive halo in GS compared to POFA between the specified 2-theta angles. The crystalline phase or peaks in GS included spinel (S), alite (A), belite (B), larnite (L) and quartz (Q) while the peaks in POFA included quartz (Q), calcite (C), cristobalite (Cr) and potassium aluminium phosphate (K₂A₂(PO₄)₃).

Table 2 presents the particle sizes of GPOFA, TPOFA, UPOFA and GS, where their median particle sizes, d₅₀ were found to be 22.55 µm, 22.51 µm, 1.069 µm and 1.098 µm, respectively. Further, thermal and grinding treatment of POFA facilitated increment in the percentage of oxide composition of SiO₂, CaO, and Al₂O₃ with the highest and lowest percentage of these mineral oxides found in UPOFA and GPOFA, respectively. Calcination process also led to the reduction in the content organic impurities, carbon content and black colorations that characterized the original POFA. **Table 3** indicates that TPOFA had a reduced median particle sizes (22.51 µm) that was slightly higher than that of GPOFA (22.55 µm) but significantly less than that of UPOFA (1.069 µm). The surface area (BET) values of TPOFA and UPOFA were 6.75 m²/g and 13.40 m²/g, respectively. Since both TPOFA and UPOFA were the products of calcined ground POFA, there carbon contents were approximately the same (~4.87%) likewise their loss on ignition (LOI) values (2.56) as shown in **Table 2**.

3.2 Influence of grades of POFA on the strength of AAG-POFA mortar

From **Table 4**, the unit weight of the alkaline activated GS-ultrafine POFA (AAG-UPOFA) was the highest (2248 kg/m³) which was 4.6% and 37.6% greater than

the unit weight values of the sample prepared with AAG-TPOFA and AAG-GPOFA mortars, respectively. This signified that the mortar prepared with UPOFA was denser than those prepared with either TPOFA or GPOFA. The compressive strength was progressively increasing from 3 days to 28 days in all the specimens. No substantial strength was observed in AAG-GPOFA mortar. The maximum early strength (3-d) recorded in AAG-UPOFA mortar was 23.3 MPa, which was about 86.6% and 13.9% of the strength achieved in AAG-GPOFA and AAG-TPOFA mortars, respectively. Similarly, the maximum 28-d strength in AAG-GPOFA mortar was 3.2 MPa, which was about 88.5% and 90.2% lesser than the strength, achieved in AAG-TPOFA and AAG-UPOFA mortars, respectively.

By comparing the strength of AAG-TPOFA with that of AAG-UPOFA, the compressive strength obtained in AAG-TPOFA at 3-d, 14-d and 28-day, were 16.3%, 10.23% and 17.24%, respectively less than the values obtained in AAG-UPOFA mortar. Therefore, the fineness of UPOFA materials and its compatibility with GS contributed significantly to the compressive strength as the rate of reaction increased with the fineness of the materials, which in turn increased with the surface areas of the reactant particles. These assertions reflected the fact that high carbon content in AAG-GPOFA had a significant debilitating effect on the density and the strength development of the product. Thus, decarbonizing palm oil fuel ash prior to its use in binary combination with GS in the development of AAB substantially enhanced its strength performance.

Besides, the progressive increase in the compressive strength observed in all the products as shown in **Table 4** implies that pozzolanic reaction followed the post-thermal curing of the mortar thereby leading to further strength development. This is possible owing to the reaction between the microstructural residual water, Ca²⁺ from PMs and the hydroxylized silicic acid (Si(OH)₄²⁻ or H₄SiO₄) formed from the dissolution reactions of alkaline activators and the base materials (Provis and van Deventer 2009; Yusuf *et al.* 2014a), which resulted in H₂SiO₄²⁻ as shown in Eqs. 1a and 1b (Georgescu *et al.* 2012).

Which can be written in short form or cement chemist notation as:

The presence of anorthite (CaAl₂(SiO₄)₂) that was found in the XRD diffractogram (**Fig. 2**) of all the speci-

Table 3 Materials physical properties.

Materials	Specific gravity	Median particle size, d ₅₀ µm	Specific surface area, S _{BET} m ² /g
POFA	2.42	41.26	2.56
GPOFA	2.52	22.55	9.02
TPOFA	2.56	22.51	6.75
UPOFA	2.60	1.069	13.40
GS	2.90	1.098	14.92

Table 4 Compressive strength, flows and unit weight for alkaline activate ground slag and palm oil fuel ash mortars.

#ID	Flow, mm (inch)	Unit weight kg/m ³	3-d Compressive strength, MPa	14-d Compressive strength, MPa	28-d Compressive strength, MPa
AAG-GPOFA	102	1402	2.75	3.0	3.20
AAG-TPOFA	112	2144	20.57	25.69	27.72
AAG-UPOFA	131	2248	23.93	28.32	32.50

Fig. 2 XRD diffractogram of pulverized mortar of alkaline activated ground slag with different grades of palm oil fuel ash.

mens indicated the possibility of the reaction that led to the formation of C-S-H with the propensity of infusion of Al (C-(A)-S-H) (Yusuf *et al.*, 2014c).

3.3 Influence of grades of POFA on the carbonation of AAG-POFA mortar

On the effects of carbon content on the nature of the products, XRD diffractograms (Fig. 2) shows the presence of calcite in all the mortars at approximately 29.5° but with the additional peak at around 36° (2-theta angle) in the diffractogram of AAG-GPOFA and AAG-TPOFA that was conspicuously visible in both than in AAG-UPOFA mortar. Therefore, it appeared that the presence of CaO in POFA contributed to the formation of calcite as shown in Eq. 2. Therefore, the removal of black carbon improved the amorphous phase and the compressive strength of the product.

The possibility of early formation of calcite as the aftermath effect of reaction of atmospheric CO_2 with CaO (Eq. 2) in the carbon-ladden binder (AAG-GPOFA) was higher compared to other low carbon products - AAG-TPOFA and AAG-UPOFA. The FTIR spectra (Fig. 3) show wavy bands in the spectra of AAG-GPOFA and AAG-TPOFA due to stretching vibration of O-C-O bond (CO_3^{2-}) at the wavenumber $1427\text{--}1486\text{ cm}^{-1}$ and $1427\text{--}1487\text{ cm}^{-1}$, respectively. The wavy peak disappeared in AAG-UPOFA spectra as the vibration occurred at wavenumber 1427 cm^{-1} . The nature of micrographs of AAG-GPOFA shown in Fig. 4A compared to the other two products signified that there could be high level of carbonation process due to its non-uniform nature of its microstructure compared to the denser AAG-UPOFA (Fig. 4B) and AAG-TPOFA (Fig. 4C) microstructure.

This pointed to the presence of less pores that might reduce the infiltration of atmospheric CO_2 in the interstices of AAG-UPOFA product matrix.

3.4. Effect of grades of POFA on the microstructures of the mortars

Change in the grade of POFA was found to significantly affect the microstructure of the mortar formed as shown in Fig. 4A-C. The AAG-GPOFA FESEM micrograph (Fig. 4A), shows a heterogeneous, dispersed and non-uniform with “spiky” outgrowth while that of AAG-UPOFA (Fig. 4B) and AAG-TPOFA (Fig. 4C) appeared compact, dense and discretely uniform. The EDS results show the different formations in the products. Regions 1 to 3 of AAG-GPOFA show significant decrease in the content of Si (5.34-11.72%), whereas the regions 4 to 6 of AAG-UPOFA (25.01-58.32%) and regions 7 to 9 of AAG-TPOFA (22.07-54.97%) indicate the presence of a significant amount of Si. The Si-O-Si bending vibration were clearly indicated in all the three samples by the FTIR spectra (Fig. 3) at wavenumber 455 cm^{-1} .

Comparison of Al/Si ratio in the EDS results of the AAG-GPOFA showed the values of 0.8, 0.094 and 0.112 in the regions 1, 2 and 3, respectively. It varied from 0.12 to 0.32 in the regions 4 and 5 of AAG-UPOFA while it varied between 0.1 to 0.2 in the regions 7 and 8 of AAG-TPOFA, respectively. Similarly, Ca/Si ratio in the regions 4 and 7 of the AAG-UPOFA and AAG-TPOFA were 0.24 and 0.40, respectively while it was 0.445, 0.52 and 3.18 in the regions 1, 2 and 3 of AAG-GPOFA. The CaO/ Na_2O in AAG-GPOFA ranged between 0.54-1.18 (region 1-3). It was however, found to be 0.875-0.896 in AAG-UPOFA (region 4-6), and in the range of 0.803-0.875 in AAG-TPOFA (region 7-9).

However, Fig. 2 shows the presence of anorthite

Fig. 3 FTIR spectra of pulverized alkaline activated ground slag-palm oil fuel ash mortar.

(C/N-A-S-H) in all the samples regardless of the type of POFA used in the synthesis but the SEM+EDS (Fig. 4A-C) show that such formation could be localized in AAG-GPOFA mortar in comparison with its wide distributions in AAG-UPOFA and AAG-TPOFA. This is due to the absence or dearth of Al and Si in certain regions. Unlike AAG-GPOFA mortar, the formation of C-(A)-S-H and C/N-A-S-H were quite possible in AAG-UPOFA and AAG-TPOFA mortar.

From Fig. 5, it is clearly shown from the specific regions of the micrographs of AAG-UPOFA and AAG-TPOFA that the products formed within the microstructure were composed of C/N-A-S-H or C-(A)-S-H solid skeletons. EDS result of region 10 of AAG-UPOFA mortar could be written empirically as $\text{Na}_{1.4}\text{Ca}_{7.0}\text{AlSi}_{10.3}$ (C/N-A-S-H) while that of region 11 could be expressed as $\text{Na}_{2.9}\text{Ca}_{47.6}\text{AlSi}_{9.7}$ (C/N-(A)-S-H). Similarly, the regions 12 and 13 of AAG-TPOFA could be simultaneously expressed as $\text{Na}_{4.97}\text{Ca}_{4.2}\text{AlSi}_{8.3}$ and $\text{Na}_{4.81}\text{Ca}_{4.6}\text{AlSi}_{10.3}$ (C/N-A-S-H). These identified products were responsible for the higher compressive strength obtained in both of them. The Si-O-Si(Al) bond vibrations in the FTIR spectra (Fig. 3) at the wavenumbers 1034 and 1069 cm^{-1} for AAG-UPOFA and AAG-TPOFA, respectively that appeared together in AAG-

GPOFA supported this argument. The lower wavenumber (1034 cm^{-1}) as observed in AAG-UPOFA indicated the attachment of either heavier metals (Ca^{2+}) to Si-O-Si(Al) thereby forming a $\text{Ca}(\text{Si})\text{-O}(\text{Si})\text{Al}$ bond or causing the replacement of Si-O due to the entry of weaker tetrahedral Al-O in IV fold coordination into Si-O-Si bonds (Lee and van Deventer 2002). Therefore, it can be said that Al was more uniformly distributed in AAG-UPOFA and AAG-TPOFA products while it appeared more localized in AAG-GPOFA.

Similarly, Mg was found absent in the EDS of AAG-GPOFA (regions 2 and 3) but not in AAG-TPOFA (regions 7 and 8) and AAG-UPOFA (regions 5). It implies that Mg might contribute to the microstructural density and since it caused formation of short-range order preferentially to Ca (Antipas *et al.*, 2012). The decreased in the compressive strength of AAG-TPOFA compared to AAG-UPOFA could result from preponderance of Mg in the regions 7 and 8 of the former as against its presence only in the region 5 of the latter. Nonetheless, the role of Mg in the strength development and the microstructure of AAG-POFA requires further investigations.

Thus, carbon content controlled the range of Ca/Si, Al/Si and CaO/ Na_2O distribution of the product rather than fineness of the base materials. However, both fine-

Fig.4A Micrographs and EDS results of alkaline activated ground slag-ground palm oil fuel ash mortar (AAG-GPOFA).

Fig.4B Micrographs and EDS results of alkaline activated ground slag-ultrafine palm oil fuel ash mortar (AAG-UPOFA).

ness of base materials and carbon content played important roles in determining the strength of the AAG-POFA mortar (Table 4).

3.5 Effects of grades of POFA on the workability and flow of the mixture

Absorption of water by carbon and organic materials in AAG-GPOFA affected the flow of mortar as shown in Table 4. The carbon content caused the reduction in the flow. The low carbon AAG-UPOFA had the highest flowability with the measured flow diameter of 131 mm, which was followed by AAG-TPOFA (112 mm), and the lowest workability was observed in the carbon-laden

AAG-GPOFA (102 mm). The content of organic materials as reflected by the loss on ignition (LOI) and carbon content (C) as shown in Table 2 enhanced water absorption through capillary action from the mixture (Yusuf *et al.* 2014d). The earlier calcite formation in (Eq. 3) increases the viscosity and loss of fluidity of the mixture. In addition, the reactivity of slag with POFA due to their fineness induced early setting especially in AAG-UPOFA and AAG-TPOFA mortars. These eventually led to the reduction of water available for lubrication of particles thereby increasing the inter-particle abrasion (Steins *et al.* 2012; Zuhua *et al.* 2009). It was clear that carbon content and particle sizes had significant effects

Fig.4C Micrographs and EDS results of alkaline activated ground slag-treated palm oil fuel ash mortar (AAG-TPOFA).

Fig. 5 Micrographs and EDS showing the specific regions within the microstructure of AAG-UPOFA (10 and 11) and AAG-TPOFA mortar (12 and 13).

on the rheology of the mixtures. Thus, the type of POFA utilized in the synthesis of AAG-POFA binder could impact their strength and workability.

3.6 Effects of grades of POFA on the amorphousness of the binders

Since higher Si-Al substitution changes the amorphousness, more of the replacement of Si with Al in IV

fold coordination to form Si-O-Al took place in AAG-UPOFA than in AAG-GPOFA and AAG-TPOFA. This suggests that AAG-UPOFA was more amorphous than the AAG-GPOFA and AAG-TPOFA mortar. This assertion corroborates the higher percentage composition of Al in AAG-UPOFA (regions 4, 5 and 6) as shown in the SEM+EDS compared to AAG-GPOFA (regions 1, 2 and 3) and AAG-TPOFA (regions 7, 8 and 9) as shown in

Fig. 4A-C. The broader nature of the peak 1034 cm^{-1} in AAG-UPOFA suggested that it was more amorphous than AAG-GPOFA and AAG-TPOFA (**Fig. 3**). From the XRD diffractogram in **Fig. 2**, all the products contained anorthite (C-A-S-H) but it appeared that such formation was more amorphous in AAG-UPOFA than that of AAG-GPOFA and AAG-TPOFA. Therefore, the fineness of the base materials - as noticed in the comparison of AAG-UPOFA with AAG-TPOFA - could change the degree of amorphousity of the products. Similarly, the presence of calcite in the product of all the samples also reflected in the FTIR spectra in **Fig. 3** by the vibration band at wavenumber 2926 cm^{-1} (Sakulich, 2009). The disappearance of calcite at 2-theta angle of approx. 36° in the XRD signified that the calcite in AAG-UPOFA could be more amorphous than that of the other two products.

4. Conclusions

Different grades of palm oil fuel ash namely: ground palm oil fuel ash (GPOFA), calcined or treated GPOFA (TPOFA), and ground TPOFA or ultrafine POFA (UPOFA) had been used in binary blending with ground slag to study the potency of their reactivities in the synthesis of alkaline activated GS-POFA mortar (AAG-POFA). The findings showed that the grades gave different responses in terms of strength, workability and amorphousity while the following were the conclusions:

- 1) Calcination of palm oil fuel ash (POFA) reduced its carbon content and loss on ignition while milling reduced its particle sizes, increased its surface areas and enhanced their oxides composition (CaO , SiO_2 , Al_2O_3 and MgO).
- 2) Unburned carbon, fineness and surface areas play significant roles in the synthesis of AAG-POFA mortar of good workability (consistency).
- 3) Carbon content controlled the range of Ca/Si , Al/Si and $\text{CaO/Na}_2\text{O}$ distribution of the product rather than fineness of base materials. However, both fineness of base materials and carbon content played important roles in determining the strength of the AAG-POFA mortar
- 4) AAG-UPOFA mortar had the best compressive strength, unit weight, microstructural density and amorphousity in comparison with mortar synthesized using AAG-TPOFA and AAG-GPOFA.
- 5) GPOFA could not generate adequate structural strength when used for the synthesis of AAG-POFA mortar. However, TPOFA and UPOFA could be successfully utilized in the synthesis. Therefore, the cost of energy required for the processing of TPOFA to produce UPOFA could be conserved by utilizing the former in the synthesis, however with a trade off in the compressive strength.

Acknowledgements

The authors gratefully acknowledge the Universiti Sains Malaysia for providing the financial support through the

Research University Grant Scheme (1001/PAWAM/814191) for undertaking the research work. The supports from Centre for Engineering Research, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia are specially acknowledged. Thanks are also due to United Palm Oil Industries and Southern Steel Company for providing the palm oil fuel ash and steel slag, respectively.

References

- Antipas, G. S. E., Temleitner, L., Karalis, K., Kohara, S., Pusztai, L. and Xenidis, A., (2012). "A containerless study of short-range order in high-temperature Fe-Si-Al-Ca-Mg-Cr-Cu-Ni oxide systems." *Journal of Molecular Structure*, 1019, 151-158.
- ASTM: C-1437, (2013). "Standard test method for flow of hydraulic cement mortar." American Society for Testing and Materials, ASTM International, West Conshohocken, PA, www.astm.org.
- Budiea, A., Hussin, M. W., Muthusamy, K. and Ismail, M. E., (2010). "Performance of high strength POFA concrete in acidic environment." *Concrete research letters*, 1, 14-18.
- Chandara, C., Sakai, E., Mohd, Azizli, K. A., Ahmad, Z. A. and Saiyid, Hashim, S. F., (2010). "The effect of unburned carbon in palm oil fuel ash on fluidity of cement pastes containing superplasticizer." *Construction and Building Materials*, 24, 1590-1593.
- Chindaprasirt, P., Homwuttiwong, S. and Jaturapitakkul, C., (2007). "Strength and water permeability of concrete containing palm oil fuel ash and rice husk-bark ash." *Construction and Building Materials*, 21, 1492-1499.
- Davidovits, J., (1999). "Chemistry of Geopolymeric Systems, Terminology." In: Géopolymère'99, 2nd International Conference, Saint-Quentin, France, 9-40.
- Georgescu, M., Mohanu, I., Voicu, G. and Cotofana, V., (2012). "Physical-chemical processes at hardening of some lime-limestone-volcanic tuff composites." *UPB Scientific Bulletin, Series B: Chemistry and Materials Science* 74.
- Huntzinger, D. N. and Eatmon, T. D., (2009). "A life-cycle assessment of cement manufacturing: comparing traditional process with alternative technologies." *J. Clean Prod*, 17, 668-675.
- Hussin, M. W. and Abdul Awal, A. S. M., (1998). "Influence of palm oil fuel ash on sulfate resistance of mortar and concrete." *American Concrete Institute, SP. 178*, 417-430.
- Jaturapitakkul, C., Tangpagasit, J., Songmue, S. and Kiattikomol, K., (2011). "Filler effect and pozzolanic reaction of ground palm oil fuel ash." *Construction and Building Materials*, 25, 4287-4293.
- Karim, M. R., Zain, M. F. M., Jamil, M., Nazrul Islam, M., (2011). "Strength of concrete as influenced by palm oil fuel ash." *Australian Journal of Basic and Applied Sciences*, 5, 990-997.
- Kroehong, W., Sinsiri, T. and Jaturapitakkul, C., (2011a).

- "Effect of palm oil fuel ash fineness on packing effect and pozzolanic reaction of blended cement paste." *Procedia Engineering*, 14, 361-369.
- Kroehong, W., Sinsiri, T., Jaturapitakkul, C. and Chindaprasirt, P., (2011b). "Effect of palm oil fuel ash fineness on the microstructure of blended cement paste." *Construction and Building Materials*, 25, 4095-4104.
- Lee, W. K. W. and van Deventer, J. S. J., (2002). "The effects of inorganic salt contamination on the strength and durability of geopolymers." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 211, 115-126.
- Li, C., Sun, H. and Li, L., (2010). "A review: The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements." *Cement and Concrete Research*, 40, 1341-1349.
- Manso, J. M., Losanez, M., Polanco, J. A. and Gonzalez, J. J., (2005). "Ladle furnace slag in construction." *Journal of Material in Civil Engineering (ASCE)*, 17, 513-518.
- Megat Johari, M. A., Brooks, J. J., Kabir, S. and Rivard, P., (2011). "influence of supplementary cementitious materials on engineering properties of high strength concrete." *Construction and Building Materials*, 25, 2639-2648.
- Megat Johari, M. A., Zeyad, A. M., Bunnori, N. M. and Ariffin, K. S., (2012). "Engineering and transport properties of high-strength green concrete containing high volume of ultrafine palm oil fuel ash." *Construction and Building Materials*, 30, 281-288.
- Meyer, C., (2009). "The greening of the concrete industry." *Cement Concrete Composites*, 31, 601-605.
- MPOB, (2013). "Malaysia Oil Palm Statistics." 2007. http://econ.mpob.gov.my/economy/annual/stat2007/EID_statistics07.htm. [accessed: 24-09-2013].
- Pacheco-Torgal, F., Castro-Gomes, J. and Jalali, S., (2008). "Alkali-activated binder: a review, part 1: historical background, terminology, reaction mechanism and hydration products." *Construction and Building Material*, 22, 1305-1314.
- Provis, J. L., van Deventer, J. S. J., (2009). "Geopolymers: structure, processing, properties and industrial applications." Woodhead Publishing Limited.
- Sakulich, R. A., (2009). "Characterization of Environmentally-Friendly Alkali Activated Slag Cements and Ancient Building Materials." Materials Science and Engineering. Drexel University, Philadelphia, USA, 1-198.
- Shi, C., (2002). "Characteristics and cementitious properties of ladle slag fines from steel production." *Cement and Concrete Research*, 32, 459-462.
- Steins, P., Poulesquen, A., Diat, O. and Frizon, F., (2012). "Structural evolution during geopolymerization from an early age to consolidated material." *Langmuir : the ACS journal of surfaces and colloids*, 28, 8502-8510.
- Tay, J. H., (1990). "Ash from oil-palm waste as concrete material." *Journal of Materials in Civil Engineering*, 2, 94-105.
- Warren, P. L. and Shadforth, P. Y., (1999). "Scope and limitation for semi-quantitative XRF analysis." JCPDS International Centre for Diffraction Data 783-786.
- Yusuf, M. O., Megat Johari, M. A., Ahmad, Z. A. and Maslehuddin, M., (2014a). Effects of H₂O/Na₂O molar ratio on the strength of alkaline activated ground blast furnace slag-ultrafine palm oil fuel ash based concrete." *Materials & Design*, 56, 158-164.
- Yusuf, M. O., Megat Johari, M. A., Ahmad, Z. A. and Maslehuddin, M., (2014b). "Evolution of alkaline activated ground blast furnace slag-ultrafine palm oil fuel ash based concrete." *Materials & Design*, 55, 387-393.
- Yusuf, M. O., Megat Johari, M. A., Ahmad, Z. A. and Maslehuddin, M., (2014c). "Strength and microstructure of alkali-activated binary blended binder containing palm oil fuel ash and ground blast-furnace slag." *Construction and Building Materials*, 52, 504-510.
- Yusuf, M. O., Megat Johari, M. A., Ahmad, Z. A., Mohammed, M., (2014d). "Shrinkage and strength of alkaline activated ground steel slag/ultrafine palm fuel ash pastes and mortars." *Materials and Design*, 63, 710-718.
- Zuhua, Z., Xiao, Y., Huajun, Z. and Yue, C., (2009). "Role of water in the synthesis of calcined kaolin-based geopolymer." *Applied Clay Science*, 43, 218-223.