Performance of POFA-Based Alkali-Activated Mortar Exposed to Elevated Temperatures

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ABSTRACT. This research work was conducted to investigate the residual strength performance of POFA alkali-activated mortar when subjected to different levels of elevated temperature. 100% POFA, sand and ($Na_2SiO_{3(aq)}/NaOH_{(aq)}$) ratios of 2.5, 2, 1 and 0.5 were used in the preparation of POFA alkali-activated mortar mixtures. 50 mm x 50 mm x 50 mm cube specimens were tested after 60±5 °C heat curing to study the effect of exposure to 3 levels of elevated temperature; 300, 600 and 900 °C. The performance metrics used to assess the impact of exposure to elevated temperatures were the residual compressive strength, weight loss and visual appearance. The alkaline activator ratio and the elevated temperature have induced specific impact on the residual compressive strength of the POFA alkali-activated mortar specimens. For all alkaline-activator ratios, increased strength was recorded for the specimens exposed to 600 °C temperature, however for mortar specimens exposed to 300 °C and 900 °C temperatures strength reduction was recorded. Microstructural changes of the POFA-alkali activated binder was investigated using scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS) as a result of the elevated temperature exposure. Superior performance of the 600 °C specimens was also revealed as a result of the post-heating solidification of molten POFA alkali-activated binder.

Keywords: Palm oil fuel ash (POFA), Alkali-activated binder, Elevated temperature;

1. INTRODUCTION

Alkali-activated binder, an environmentally sustainable material, recently attained the status of accepted engineering binding material. It is an engineering or scientific term used to describe inorganic polymers that are based on aluminosilicates produced from the synthetic interaction between pozzolanic materials or compounds (geopolymeric precursor) with alkaline solution [1]. Materials coming from solid wastes and by-products endowed with silica and/or alumina such as fly ash qualifies as a pozzolanic component of geopolymerization [2]. Generally, geopolymers are known to be energy efficient and good in resisting fire

because of very close semblance of their properties to ceramics. They harden at ambient temperatures, yet are sufficiently durable and stable at high temperatures. Hence, the concrete produced through the process of geopolymerization might possess higher resistance against fire compared to the ordinary portland cement (OPC) concrete [1,3]. These properties allow for their use in buildings, especially in cases of insulation against fire. When compared to conventional organic polymers, glass, ceramic, or cement, geopolymers are non-combustible, heat-resistant, formed at low temperatures, and fire/acid resistant [3]. Previous works have studied the responses of geopolymer when subjected to elevated temperature using materials such as metakaolin [4,5], fly ash [6,7], and granulated blast furnace slag [3] etc.

For this study, geopolymer mortar was produced using palm oil fuel ash (POFA), an agricultural ash residue of palm oil mill, obtained from the burning of palm fibres and palm kernel shells at temperature of about 800 - 1000 ^{o}C to produce steam for electricity generation in biomass thermal power plants. This geopolymer mortar was achieved by mixing the POFA with alkaline activated solution (NaOH$_{aq}$ and Na$_2$SiO$_{3aq}$) in the presence of sand to form mortar and actively transforms into hardened geopolymer. This was subsequently subjected to elevated temperature. Researchers have always used residual compressive strength as a mechanism to study the response of geopolymer concrete under elevated temperature. Mohammad et al. [8] studied the residual compressive strength of concrete produced from 20% replacement of cement by weight with POFA. The prepared samples were exposed to elevated temperatures of 100, 300, 500 and 800 ^{o}C and were cooled after by two systems – room temperature by natural breeze and water spray. It was found out that the POFA concrete performed better with higher residual strength than normal concrete. In addition, the high temperature and cooling systems affected greatly the mass, color and patterns of crack of the concrete containing POFA.

Compressive strength and microstructure of geopolymer mortar containing POFA subjected to elevated temperature were also studied by Ranjbar et al. [6]. POFA replaced fly ash in succession of 25% until the 100% POFA content and subjected to four levels of elevated temperatures 300, 500, 800 and 1000 ^{o}C. The study revealed that all specimens lost their strength when exposed to temperature above 500 ^{o}C. The high POFA specimens deformed when subjected to temperature above 800 ^{o}C while the FA specimens maintained thermal stability. In previous studies, geopolymer with partial replacement of portland cement, fly ash, metakaolin or granulated blast furnace slag by POFA have been used to study elevated temperature effects on the produced concrete or mortar. However, in this present study, the developed geopolymer mortar was synthesized from 100% POFA.

The objective of this study is to investigate experimentally, the performances of POFA-based geopolymer mortar and their response to three elevated temperatures at 300 ^{o}C, 600 ^{o}C and 900 ^{o}C. Room temperature was used as reference to investigate the compressive strength and microstructural characteristics of the POFA-based geopolymer mortar.

2. MATERIALS AND METHODS

2.1 *Palm Oil Fuel Ash (POFA).* Untreated raw POFA was collected from local palm oil mill. The raw POFA was dried in an oven at 100 + 5 °C for 24 hours to remove its moisture and then sieved using a set of sieves (600 µm, and 300 µm) to remove unburnt materials coarser than 300 µm. The ash obtained after sieving was ground in a mechanical ball mill with capacity of 150 balls of different sizes (6 mm to 32 mm) and a rotating speed of 180 rpm, to reduce its particle size and improve its reactivity. To remove unburned carbon and prevent glassy phase crystallization, in addition to agglomeration of particles, POFA was calcined using low heat treatment (550 °C for 90 min). To further improve the surface area, the calcined POFA underwent another round of grinding in the ball mill. The loss on ignition (LOI) values before and after heat treatment is 21.60 and 2.3%, respectively. The reduction in the LOI value is compensated for, by the increase in mass percentages of other oxide components. With total oxides of silicon, aluminium and iron of 78.07%, it complies with the specification of ASTM C618 class F. The particle size distribution of the final stage of preparation of POFA was determined using Turbotrac S360 particle size analyser (PSA). The surface areas
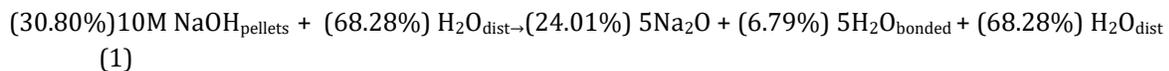
were determined using Micromeritics ASAP2020 BET using nitrogen gas adsorption. Specific surface area of POFA after treatment was 1.5 m^{2}g^{-1} with average particle size of 2.97 μm. Table 1 shows the oxide compositions of POFA, which were determined using x-ray fluorescence (XRF) technique.

2.2 Aggregates. Fine aggregate (FA) used in the study is dune sand of fineness modulus of 1.85 and specific gravity in the saturated and surface dry (SSD) condition is 2.62.

Table 1 Chemical composition and physical properties of POFA

Chemical composition (mass%)	POFA
Silicon dioxide (SiO_2)	66.91
Aluminum oxide (Al_2O_3)	6.44
Ferric oxide (Fe_2O_3)	5.72
Calcium oxide (CaO)	5.56
Magnesium oxide (MgO)	3.13
Sodium oxide (Na_2O)	0.19
Potassium oxide (K_2O)	5.20
Sulfur oxide (SO_3)	0.33
LOI	2.3
Physical properties	
Specific gravity (g/cm^3)	2.53
Median particle size d50 (μm)	2.96
Specific surface area (m^2/g)	1.521

2.3 Synthesis of alkali-activators (AA). Commercially available $Na_2SiO_{3(aq)}$ of initial silica modulus (Ms = SiO_2/Na_2O) of 3.3 and $NaOH_{(aq)}$ of 10M concentration were used as alkali-activators (AA). The constituent percentage of Na_2SiO_3 $_{(aq)}$ are as follows: H_2O:62.11%, SiO_2:29.13% and Na_2O:8.76% and constituent percentage of 10 M $NaOH_{(aq)}$ is as shown in Eq 1.

$$(30.80\%)10M\ NaOH_{pellets} + (68.28\%)\ H_2O_{dist \rightarrow}(24.01\%)\ 5Na_2O + (6.79\%)\ 5H_2O_{bonded} + (68.28\%)\ H_2O_{dist}$$
(1)

All the available water was from added free water and water contained in the AA. The distilled water and NaOH pellets of 99% purity were used in the preparation of the 10M $NaOH_{(aq)}$. The mass of solids (pellets) used is 399.98 g in 1 L of solution.

2.4 Superplasticizer. A commercially available superplasticizer satisfying the ASTM C494 Type F requirements was used to achieve adequate rheological properties in the fresh mortar as POFA is highly hydrophobic.

2.5 Mixture design. The AA to binder ratio was kept at 0.5 for all the mixtures. The total silica modulus (Ms = SiO_2/Na_2O) was obtained from activator's relative proportion – ($Na_2SiO_{3(aq)}$/10M $NaOH_{(aq)}$) such as 71.43/28.57 with an equivalent ratio of 2.5:1. The proportion of the mixtures are given in Table 2.

Table 2 POFA-ECC alkali-activated mortar mixture proportions

Specimen Designation	POFA (kg/m³)	Sand (kg/m³)	Free water (kg/m³)	Alkaline to POFA ratio	Total alkaline liquid (kg/m³)	10M $NaOH_{aq}$ (kg/m³)	Na_2SiO_{3aq} (Ms = 3.3) (kg/m³)	SP (kg/m³)
$AP_{0.5}H_{10}S_{2.5}$	676.5	1217.6	67.647	0.5	338.235	96.634	241.601	67.647
$AP_{0.5}H_{10}S_{2.0}$	676.5	1217.6	67.647	0.5	338.235	113.884	224.351	67.647
$AP_{0.5}H_{10}S_{1.0}$	676.5	1217.6	67.647	0.5	338.235	169.118	169.117	67.647
$AP_{0.5}H_{10}S_{0.5}$	676.5	1217.6	67.647	0.5	338.235	225.501	112.734	67.647

2.6 Specimen preparations. To remove air pockets, which might affect the properties of the mixture, the POFA and the sand were thoroughly mixed together. AA (mixture of $Na_2SiO_{3(aq)}$ and $NaOH_{(aq)}$ was added subsequently, allowed to mix for five mins and then followed by the water and superplasticizer, which was left to mix for another 4-5 min. The overall mixing time was approximately 12 min and the flowability of the fresh mortar was examined using the flow table test. The mixtures were cast in two equal layers into 50 x 50 x 50 mm oil-smeared cube molds and vibrated for 15 s. The samples were demolded after 12 hours in the laboratory covered in vinyl bags to prevent moisture loss. The demolded samples were placed in sealed vinyl bags undisturbed and subjected to 60±5 °C curing for 24 hours. After cooling down from curing, the physical properties like weights and densities were recorded. The control specimens were tested for compressive strength after 7 days of casting and oven curing. The compressive strength test was done using the MATEST crushing test machine of model C-99 at the loading rate of 0.9 kN/s. The other specimens were subjected to elevated temperature at 300, 600 and 900 °C, thereafter tested for residual compressive strength.

2.7 Curing regime and elevated temperature. The specimens were left to harden after casting, covered in polythene bags for 24 hours at 25 °C before subjecting to heat curing at 60±5 °C for a another 24 hours. After that, the specimens were demolded and physical properties were observed and recorded. The hardened specimens apart from the control specimens were exposed to selected elevated temperatures of 300 °C, 600 °C and 900 °C at an incremental rate of 4.4 °C/min using a 1200 °C-capacity electrically operated furnace. These temperatures were sustained for 2 hours before the specimens were allowed to cool down naturally in the furnace in order to prevent the specimen from thermal shock. The specimens were visually observed for any physical change, weighed and their residual compressive strength measured as discussed earlier.

2.8 Microstructural Investigation. To better understand the behaviour of the specimens after subjecting to elevated temperature, microstructural study of the developed POFA alkaline-activated mortar was conducted. Scanning electron microscopy (SEM) imaging equipped with energy dispersive spectrometry (EDS) was performed to understand the microstructural changes in the specimens at different exposure temperature. The phase composition and the crystalline content of the alkaline-activated mortar were also investigated using x-ray diffraction (XRD) test. In addition, thermogravimetric analysis (TGA/DSC) was performed on the treated POFA to assess its stability under thermal stress.

3. RESULTS AND DISCUSSIONS

3.1 Thermal analysis of POFA. The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves for POFA are shown in Fig. 1. From the figure, the TG curve illustrates a very slow decrease in mass until it reached 727 °C. This indicates a highly thermally stable material whose mass loss stabilizes after 1100

^{o}C. The thermal performance of POFA as base material in POFA alkali-activated binder is important in order to ascertain its stability when subjected to elevated temperature. A low thermal degradation of POFA especially up to 700 ^{o}C at 3% weight loss is an important finding as the exothermic peak temperature of OPC was reported [9] to be between 100 ^{o}C - 170 ^{o}C, a value far lower than that of POFA.

3.2 Compressive strength of POFA alkali-activated mortar. The compressive strength of hardened POFA alkali-activated mortar specimens before and after exposure to 300, 600 and 900 ^{o}C-elevated temperature are shown in Fig. 2. A clear dependence of the specimen's compressive strength on the alkaline activator (AA) ratio was established in the plot where strength increases with the increase in the AA ratio for all unexposed (control) specimens. This is because of increased generation of SiO_2 species as the alkaline ratio increases, which not only increase the SiO_2/Al_2O_3 ratio but also increases the Si-O-Si bonds. A relatively low strength recorded with the POFA alkali-activated mortar specimens was as a result of its low alumina content. This limits the amount of aluminate bridges between the silicate species that can be achieved in order to form a good strength aluminosilicate gel. A closer look at Fig. 2 revealed a decrease in strength of the 300 ^{o}C and 900 ^{o}C specimens in comparison with the control specimens. In the case of 300 ^{o}C mortar specimens, the low residual strength was due to loss of chemically bound fluid from the matrix of the POFA alkali-activated mortar due to heat. However, the heat was inadequate for the matrix to proceed into the molten phase, hence resulting in the non-homogenous appearance of the matrix. As shown in the SEM micrograph, there is a clear interphase between the solid and some of the partially formed molten phases. This brought to the matrix some weaknesses, and as a result, there was loss of strength in the POFA alkali-activated mortar specimens.
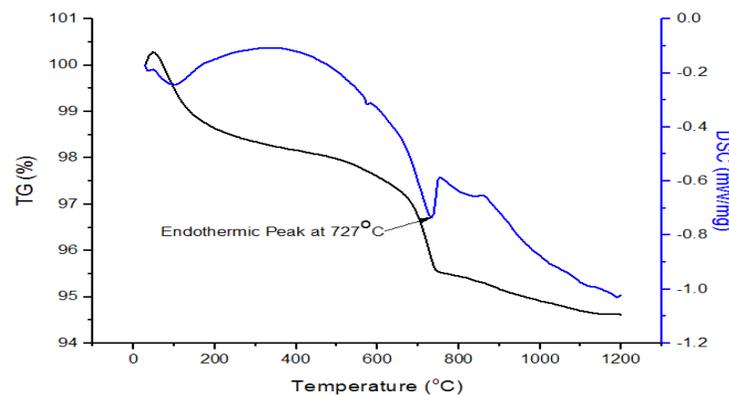
Fig. 1 TGA/DSC thermogram of palm oil fuel ash (POFA)

The highpoint of this work is the increase in strength recorded with the 600 ^{o}C elevated temperature mortar specimens in all cases of AA ratio. This temperature is taken as the optimum temperature, before and after which, there was a reduction in the compressive strength of the exposed specimens in comparison with the unexposed (control) specimens. The increase in residual strength of the 600 ^{o}C elevated temperature mortar specimens is due to the microstructural strengthening by the molten phase formation at that temperature, which hardens after cooling and gives some strength to the matrix as revealed in the SEM images (Fig. 3). This molten aluminosilicate product creates a homogenous POFA alkali-activated binder matrix, which crystallizes to improve the microstructure, hence increase the strength of the alkali-activated mortar.

As for the 900 ^{o}C mortar specimens, there was a huge decomposition of the molten phases formed at 600 ^{o}C elevated temperatures, leading to microstructural coarsening of the POFA alkali-activated mortar matrix. This

destruction of the POFA alkali-activated products leads to higher microstructural particle grains, hence, highest loss in residual compressive strength.
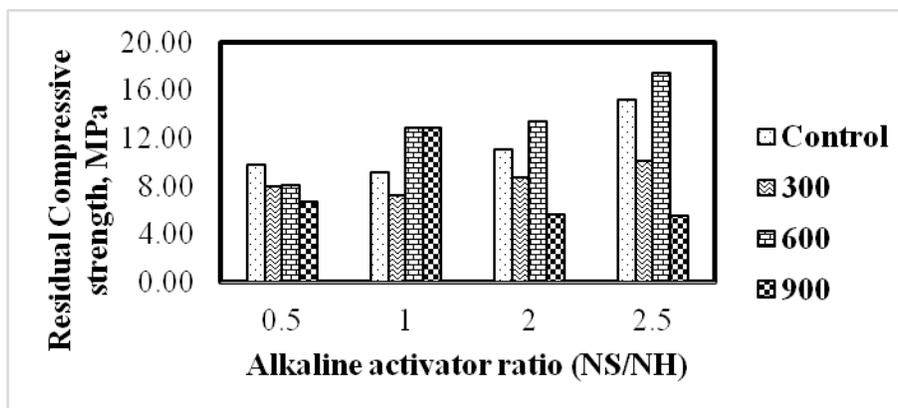

Fig. 2 Compressive strength of POFA alkali-activated mortar at 300, 600 and 900 ºC specimens
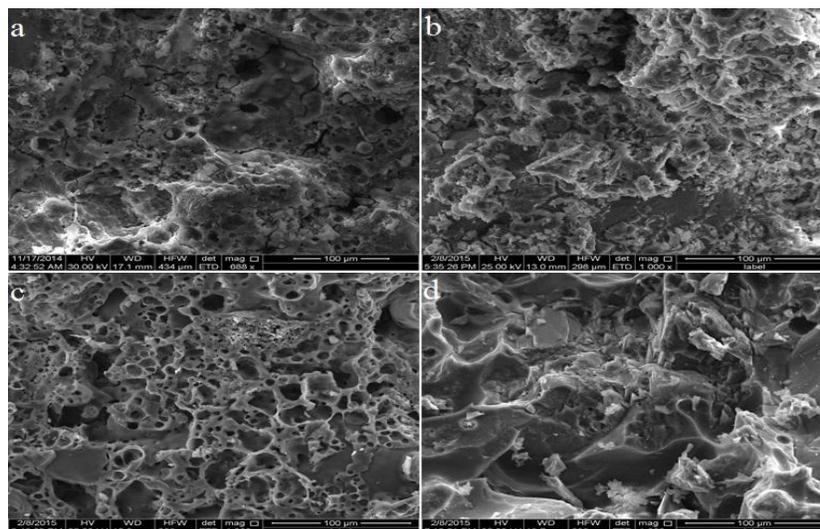

Fig. 3 SEM micrographs of specimens (a) Unexposed, (b) 300 ºC, (c) 600 ºC and (d) 900 ºC

4.   SUMMARY

The following conclusions were drawn from the study on the response of POFA alkali-activated mortar to elevated temperature. The POFA alkali-activated mortar specimens responded differently to the different levels of elevated temperature. At 300 ºC elevated temperature, there was a loss in compressive strength of the POFA alkali-activated mortar specimens due to loss of chemically bound water to heat leaving behind empty pores. This led to shrinkage and cracks within the matrix framework. There was an increase in compressive strength at 600 ºC for the POFA alkali-activated mortar specimens in all AA ratios. This is due to the microstructural strengthening by the molten phase formation at that temperature, which hardens after cooling and gives some strength to the matrix. There was a huge loss in compressive strength for the POFA alkali-activated mortar specimens exposed to 900 °C due to decomposition of the molten phases formed at 600 ºC elevated temperatures leading to the weakening of the matrix of the mortar specimens.

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