EFFECT OF WATER-BINDER RATIO AND TREATED PALM OIL ASH (TPOFA) ON ALKALI-SILICA REACTION RESISTANCE OF ENGINEERED CEMENTITIOUS COMPOSITES (ECC)

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Abstract—**This paper reports the durability performance of engineered cementitious composites (ECC) containing high volume of palm oil fuel ash (POFA) when subjected to accelerated alkaline environmental conditions. Three sets of ECC mixtures with water–binder ratios of 0.33, 0.36, and 0.38 were prepared, and for each set, the ECC mixtures were proportioned to have varying POFA contents equaling to 0, 0.2, 0.4, 0.8, and 1.2 from the mass of cement. The ECC bars were cured in water at 80 °C for 24 h. After initial reading of the lengths, the ECC bars were immersed in 1 mol sodium hydroxide (NaOH) solution at 80 °C. The expansion of the ECC bars was recorded up to 30 days. The alkali silica reaction was monitored for 3, 5, 10, 14, 20, 25, and 30 days. The test results show increasing POFA content is shown to have a negative effect in terms of ASR, but the length change due to ASR of POFA-ECC was within the limits of ASTM C1260.**

Key Words— **Engineered Cementitious Composites; Palm Oil Fuel Ash; alkali-silica reaction.**

I. INTRODUCTION

Pozzolanic materials mostly improve the mechanical properties and durability of concrete when they are used as partial replacement of cement. Palm oil fuel ash (POFA) is one such material being used as partial cement replacement because of its pozzolanic properties [1-3]. The partial replacement of Portland cement with POFA can lower production costs and improve the engineering properties and durability of concrete. Furthermore, POFA can increase the ecological properties of concrete, contributing to a healthier and more sustainable environment.

Recently, many cementitious composite materials have been developed for potential civil engineering applications. Amongst these, Engineered Cementitious Composite (ECC) represents a unique type of high performance fiber reinforced cementitious composite (HPFRCC). ECC exhibits a remarkable tensile strain capacity although it uses only short fibers with a moderate volume fraction of typically around 2 % or less [4]. The tensile strain capacity of ECC ranges from 3% to 7% [5,6].The tensile strain capacity of ECC can reach up to several hundred times that of normal concrete and FRC [7]. ECC exhibits a behavior similar to aluminum alloys due to its tensile strain-hardening behavior after a matrix first cracking, which is achieved through sequential development of multiple cracking with crack widths below 100 μm [8]. Coarse aggregates are eliminated in the ECC mixture, resulting in higher cement content compared with conventional concrete. High cement content generally introduces higher shrinkage, heat of hydration, and cost. Moreover, high cement content leads to an increase in greenhouse gas emission, which is highly relevant to global warming. A plausible solution would be to replace a large portion of the cement in ECC by an industrial by-product, without sacrificing its mechanical properties, in general, and tensile ductility, in particular.

Previous research has developed green ECCs incorporating different proportions of treated palm oil fuel ash, with a POFA/C ratio up to 1.2. It is revealed that a high volume of POFA tends to reduce the polyvinyl alcohol (PVA) fiber/matrix interface bond and matrix toughness in favor of attaining high tensile strain capacity, reducing the crack width in POFA-ECC. Incorporating high volumes of POFA in ECC generally reduces the free drying shrinkage. POFA-ECC specimens exhibited strong evidence of self healing, making them able to carry considerable tensile stress after exposure to 3 % NaCl solution [9-11].

Fracture toughness of matrix and fibre/matrix interfacial bond strength are some of the micro-mechanical parameters that govern the composite performance of ECC. These parameters may be sensitive to environmental exposure conditions [12]. One of the environments that could affect composite properties of ECC is a high alkaline environment. ECC can come into contact with alkaline media through interaction with a variety of alkaline chemicals, soil and sea water [13]. ECC structural members may be exposed to high alkaline environments and alkalis will penetrate through ECC members which could lead to modifications in the material microstructure and hence could lead to changes in the composite properties. Due to the delicate balance of matrix, fibre, and matrix/fibre interfacial properties, the strain capacity of ECC may change under high alkaline exposure conditions. Therefore, the ability of POFA-ECC composite to resist alkali silica reaction must first be evaluated before using it in real field conditions. Thus, these experimental results, taken together, provide useful information on the durability of ECC under high alkaline environment.

II. EXPERIMENTAL INVESTIGATIONS

A. Materials

POFA was collected from a nearby palm oil mill, United Oil Palm Industries Sdn. Bhd. in Nibong Tebal, Penang, Malaysia. The POFA was dried in an oven at 100°C and then sieved using a set of sieves (3 mm, 600 μm, and 300 μm). Then, the ash was ground by a ball mill to improve its reactivity. To remove unburned carbon and prevent glassy phase crystallization, POFA was heated using low heat

treatment at 450°C for 90 min. Specific surface area of POFA after treatment was 1.5 m²/g with average particle size of 2.97 µm. Other materials used in this study were ordinary Portland cement (OPC)with a specific gravity of 3.14and Blaine fineness of 340 m²/kg, silica sand (S) with average and maximum grain sizes of 110 and 200 µm, respectively, water, polyvinyl alcohol(PVA) fibres with a diameter and length of 39 µm and 8mm, respectively, hydroxypropyl methyl cellulose (HPMC) as a dry viscosity enhancing agent(to modify the workability and to achieve consistent rheological properties) and superplasticizers (SP).The chemical compositions of OPC, silica sand and treated POFA are tabulated in Table I. The mixture proportions of the ECCs used in this study are given in Table II.

TABLE I. CHEMICAL COMPOSITIONS AND PHYSICAL PROPERTIES OF USED MATERIALS

Chemical and Physical Properties	OPC	silica sand	POFA
Chemical Compositions (mass %)			
SiO_2	20.9	99.2	66.9
Al_2O_3	5.27	0.02	6.44
Fe_2O_3	3.1	0.01	5.72
CaO	62.8	-	5.56
MgO	1.52	-	3.13
Na_2O	0.16	-	0.19
K_2O	0.63	-	5.20
SO_3	2.73	-	0.33
P_2O_2	0.13	-	3.72
LOI	0.87	-	2.3
Physical properties			
Specific gravity (kg/m³)	3.14	2.6	2.53
Median particle sized_{50}(µm)	6.74	110	2.96
Specific surface area(m²/g)	0.794	0.04	1.52
Strength activity index at 7 days (%)	-	-	97.6
Strength activity index at 28 days (%)	-	-	100.7

TABLE II. MIX PROPORTION OF POFA-ECCs

Mix ID	C/C	S/C	w/b	POFA/C	SP/C	HPMC/C	Fiber
Ma1	1	0.8	0.33	0	0.022	0.001	0.02
Ma2	1	0.8	0.33	0.2	0.022	0.001	0.02
Ma3	1	0.8	0.33	0.4	0.022	0.001	0.02
Ma5	1	0.8	0.33	0.8	0.025	0.001	0.02
Ma6	1	0.8	0.33	1.2	0.03	0.001	0.02
Mb1	1	0.8	0.36	0	0.019	0.001	0.02
Mb2	1	0.8	0.36	0.2	0.019	0.001	0.02
Mb3	1	0.8	0.36	0.4	0.019	0.001	0.02
Mb5	1	0.8	0.36	0.8	0.021	0.001	0.02
Mb6	1	0.8	0.36	1.2	0.027	0.001	0.02
Md1	1	0.8	0.38	0	0.015	0.001	0.02
Md2	1	0.8	0.38	0.2	0.015	0.001	0.02
Md3	1	0.8	0.38	0.4	0.018	0.001	0.02
Md5	1	0.8	0.38	0.8	0.02	0.001	0.02
Md6	1	0.8	0.38	1.2	0.025	0.001	0.02

B. Test procedures

Accelerated mortar bar test was performed to investigate the potential durability of POFA-ECCs in alkaline environment. To measure the expansion due to highly alkaline environment, ECC mixtures as illustrated in Table II were prepared. For each ECC mixture, four ECC bar samples with dimensions of 25 mm × 25 mm × 285 mm were cast and tested according to ASTM C1260. The ECC bars were demoulded after 24 h and then cured in water at 80°C for another 24 h. After taking the initial length reading, the ECC bars were immersed in 1 mol sodium hydroxide (NaOH) solution at 80°C. The solution was made by adding 40 g of sodium hydroxide per litre of tap water. The expansion of the ECC bars was recorded up to a period of 30 days. The subsequent readings were taken after 3, 5, 10, 14, 20, 25 and 30 days. The length change in the ECC bars was calculated according to

ASTM C490). Because temperature plays a very important role in length measurements of steel studs fixed at each end of the specimen, all the readings were captured at room temperature. The expansion of each bar was computed by subtracting the initial reading from the measured readings. A standard length (28 mm) comparator equipped with an indicator (gauge), and a reference steel bar was used to measure the change in length of the samples. The comparator gauge was graduated to read in 0.002 mm. Before each measurement, the comparator gauge was calibrated using the reference steel bar. The length of the ECC bars was measured at the specified dates. The direction of the sample at each measurement was the same. The change in length resulting from ASR can be calculated according to Equation 1. The classification ranges given in ASTM C1260 are illustrated graphically in Figure 1 by horizontal gridlines.

$$\Delta L= [(L_t-L_i)/G] \times 100 \qquad (1)$$

Where, ΔL = change in length at t age (%); L_t= comparator reading of specimen at age (t) – reference bar comparator reading at (t) age; L_i= initial comparator reading of the reference bar comparator reading, at the zero time; G = nominal gauge length, 250mm.

Fig. 1. **Classification ranges of length change stipulated by ASTM C1260.**

III. RESULTS AND DISCUSSION

Table III summarizes the expansion values of ECC bars containing different contents of POFA with different w/b ratios, until 30 days. Figures 2 to 5 illustrate the development of expansion of the ECC bars with time to demonstrate the influence of POFA on the expansion of ECC bars with w/b ratios of 0.33, 0.36 and 0.38.

TABLE III. PERCENTAGE OF LENGTH CHANGE OF ECC BARS SUBJECTED TO 1 MOL SODIUM HYDROXIDE SOLUTION

| Mix ID	3 d	5 d	10 d	14 d	20 d	25 d	30 d
				w/b= 0.33			
Ma1	-0.004	-0.003	0.0008	0.0048	0.005	0.008	0.0088
Ma2	-0.001	0.001	0.003	0.0048	0.005	0.012	0.016
Ma3	0.008	0.010	0.012	0.0208	0.036	0.0368	0.0368
Ma5	0.002	0.008	0.032	0.0328	0.056	0.076	0.096
Ma6	0.002	0.009	0.036	0.0676	0.091	0.099	0.1008
				w/b= 0.36			
Mb1	-0.003	-0.001	0.002	0.008	0.0108	0.0108	0.0112
Mb2	0.0006	0.007	0.008	0.0096	0.0152	0.0208	0.036
Mb3	0.012	0.013	0.022	0.0292	0.0536	0.0612	0.0656
Mb5	0.010	0.019	0.043	0.06	0.0832	0.0892	0.1
Mb6	0.004	0.009	0.0312	0.054	0.0708	0.0788	0.0868
				w/b= 0.38			
Md1	0.0004	0.004	0.005	0.008	0.0104	0.012	0.012
Md2	0.0008	0.003	0.009	0.0128	0.0224	0.0296	0.0384
Md3	0.008	0.010	0.028	0.0336	0.0464	0.0528	0.0576
Md5	0.005	0.020	0.046	0.066	0.0828	0.092	0.1
Md6	0.004	0.012	0.048	0.0624	0.0748	0.0904	0.1028
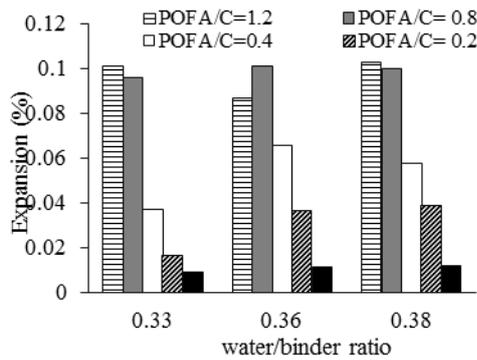
Fig. 2. **Expansion of ECC bars due to ASR at age of 30 days with different w/b and POFA/C ratios.**
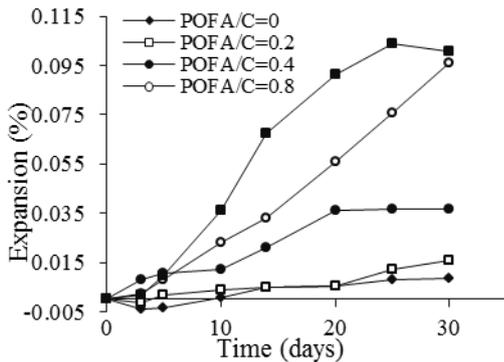

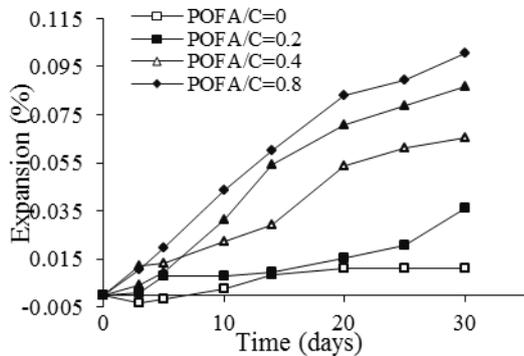Fig. 3. **Effect of POFA/C ratio on the expansion of ECC bars due to ASR at w/b= 0.33.**

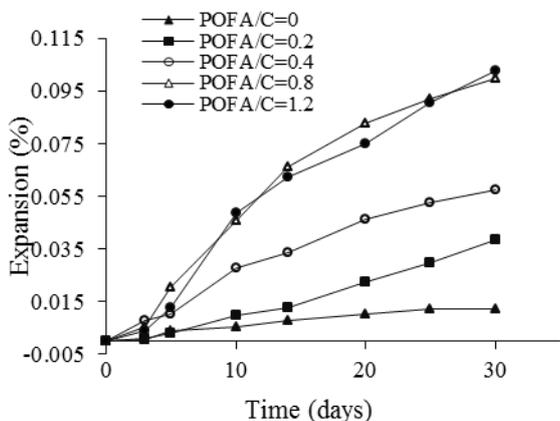Fig. 4. **Effect of POFA/C ratio on the expansion of ECC bars due to ASR at w/b= 0.36.**

Fig. 5. **Effect of POFA/C ratio on the expansion of ECC bars due to ASR at w/b= 0.38.**

Although this is traditionally a 14 days test, to obtain additional information length changes were monitored up to 30 days. ASTM C1260 standard suggested that if the measured expansion after 14 days is less than 0.1%, the ASR presumably is innocuous. However, if the expansion is more than 0.2%, the ASR is potentially deleterious. After storage of ECC bars in the 1 mol sodium hydroxide solution until 30 days, visible cracks could not be observed on the all specimens. This is because the value of expansion is very small, and the reason for this could be attributed to the use of PVA fiber in the production of ECC. Another possible reason of low expansion of ECC bars could be a result of weakness of silica sand reactivity [13].

A. Effect of water-binder ratio

It was observed that w/b ratio has a significant influence on alkali silica reaction. Increasing w/b ratio from 0.33 to o.38 results in increase the expansion at all measurement durations.ECC bars with w/b ratio of 0.38 exhibited the highest expansions followed by 0.36 and 0.33 w/b ratio. For specimens without POFA, the increasing in w/b ratio from 0.33 to 0.36 results in an increase in the expansion magnitudes by 36 % at 30 days (Fig. 2). While, the ECC bars with POFA/C ratio of 0.4, the expansion tends to increase by 55%. In addition, increase the w/b ratio from 0.33 to 0.38leads to increase the expansion by 4 % and 2 % for specimens containing POFA/C ratio of 0.8 and 1.2 respectively. The reason for this might be explained by the fact that as the w/b ratio decreased to 0.33; the porosity of ECC specimens decreases and becomes less permeable. Therefore, reducing the permeability of ECC specimens and further reduce the free movement of alkali ions causing less ASR reactivity [14]. It should be noted that until 25 days expansions for ALL ECC BAR AT ALL W/B RATIOS WERE WELL UNDER 0.10%. As a result, it can be concluded that as the w/b ratio of the ECC bars increases from 0.33 to 0.38, their expansion increases within the limits of ASTM C 1260. This indicates that the effect of ASR at 25 days is harmless.

B. Effect of POFA content

The results of the expansion tests show that the expansion increased systematically as the POFA/C ratio increased. The highest value of expansion was observed at POFA/C = 1.2, with w/b= 0.38. However, after 30 days immersing in NaOH solution at w/b= 0.33, addition of POFA at dosages of 0.2, 0.4, 0.8, and 1.2 leads to increase the expansion by 0.016%, 0.036%, 0.096% and 0.1 %, respectively(Fig. 2 and 3). At the same condition with w/b= 0.36, the increasing in expansion was 0.036%, 0.065%, 0.1% and 0.086 %(Fig.2 and 4). It can be also observed that an increase in w/b ratio up to 0.38 results in an increase in the expansion by0.038%, 0.057%, 0.1% and 0.102 % (Fig.2 and 5). At 30 days, with the exception of Md6 (w/b= 0.38 and POFA/C= 1.2), all ECC bars exhibited expansion within the limits of specifications after 14 days, as specified by ASTM C 1260 standard. In addition, the specimens without POFA (POFA/C= 0) did not show significant expansion at all ages. At 30 days, the expansion of the OPC-ECC specimens seems to be low; the expansion magnitudes were 0.008%, 0.011% and 0.012% at w/b ratio of 0.33, 0.36 and 0.38, respectively. However, this expansion is much less than those provided in the specifications after 14 days.
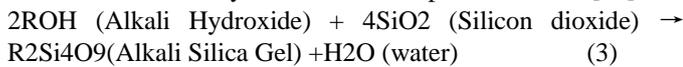
The expansion of ASR was found more closely correlated with the total alkali content. Thus, the total alkali content is expressed as sodium hydroxide equivalent (Na_2O) rather than

the individual concentrations of alkali oxides [15].The formula for calculating Na_2O equivalent is:

$$Na2O \% = Na2O \% + (0.658 \times K2O. \%) \qquad (2)$$

Where, Na_2O % is equivalent alkalizes

The expansion mechanism of ASR occurs when the siloxane networks is broken in dissolution of reactive silica or quartzin aggregate particle due to the attack of alkalis and hydroxyl ions (sodium and potassium hydroxide ions). As a result, producing an alkali-silicate gel [16]. The alkali-silicate-gel (ASG) is not expansive but this gel has a very high tendency to absorb water from the pore solution, depending on its composition, making the pore solution more alkaline resulting alkali-silicate solution or alkali-silicate-hydrate gel (N+K-S-H)swells and develops an expansive pressure, leading to expansion. The chemical equation which can be associated with this reaction may be written in simplified form as [17]:

$$2ROH \text{ (Alkali Hydroxide)} + 4SiO2 \text{ (Silicon dioxide)} \rightarrow R2Si4O9\text{(Alkali Silica Gel)} + H2O \text{ (water)} \qquad (3)$$

Where, R is any alkali (Sodium, Potassium)

From above discussion, it can be concluded that sodium and potassium play a significant role in the expansion. POFA analysis shows the presence of variable percentages of sodium and potassium oxides. The total alkali as Na_2O equivalent of POFA used in this study is 3.6%, which is much higher than the maximum limit of 1.5% prescribed in the ASTM C618 standard. Therefore, increase ASR expansion with increase the POFA contents could be due to high content of potassium oxide in the POFA, which leads to increases the pH in alkaline solution, therefore, increasing the likelihood of ASR (i.e. high K_2O, high potassium silica gels).The second reason that the POFA itself may become a source that would react with the alkalis. In other words, the silica in the POFA is found in many forms, amorphous, crystalline and semi-crystalline. Some of these forms are normally appear in the form of tridymite, cristobalite and quartz. These forms increasing with increase the amount of POFA in mix, and thus they would react with alkali hydroxide resulting in alkali silica reaction expansion.

IV. CONCLUSIONS

Based on the experimental results reported in this paper, the following conclusions can be drawn:

- At all measurement durations, increasing the w/b ratio in all ECC bars mostly tends to increase the expansion due to alkali-silica reaction. As w/b ratio of ECC bars increases from 0.33 to 0.38, the expansion increases within the limits of ASTM C 1260. Nevertheless, the negative effect of w/b ratio on ECC bars expansion was lower as POFA/C ratio increased.

- The increase of POFA content generally leads to increase the rate of expansion due to alkali-silicate reaction. However, POFA-ECC did not show considerable expansion at the end of 30 days soaking period, and this expansion is considered harmless based on ASTM C 1260 Standard Specifications.

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