

## Reduction of Alkali-Silica Reaction Expansion using Ultrafine Palm Oil Fuel Ash

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**Abstract:** This study presents the effect of Ultrafine Palm Oil Fuel Ash (UPOFA) in controlling the Alkali-Silica Reaction (ASR) expansion in mortar bar through pozzolanic reactivity, alkali binding, reduction of aggregate dissolution and change in the Alkali Silica Gel (ASG) composition. The expansion of mortar bar was investigated using the Accelerated Mortar Bar (AMBT) by replacing 10-40% of cement with UPOFA. The effects of how UPOFA reduced the ASR were then studied by conducting the pozzolanic activity test, Thermo Gravimetric Analysis (TGA), aggregate dissolution and Scanning Electron Microscopy (SEM). It was found that 20-40% UPOFA has the ability to reduce the ASR expansion in a mortar. The higher the amount of replacement, the lower the ASR expansion recorded. Strength activity index at 7 and 28 days showed higher pozzolanic reactivity indicating the formation of Extra Calcium Silica Hydrate (CSH) through pozzolanic reaction and this was supported by the TGA analysis of the CSH and Calcium Hydroxide (CH) content. The aggregate dissolution was reduced with an increment of POFA replacement level. The change in the chemical composition of the ASG indicates the transformation of the ASG characteristic from hard to soft and less vicious gel which explains the lower ASR expansion when ultrafine UPOFA was used as supplementary cementitious material in mortar bar.

**Key words:** Alkali-silica reaction, ultrafine palm oil fuel ash, mortar expansion, cementitious material, extra calcium silica hydrate, TGA

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### INTRODUCTION

Reactive aggregates used in concrete will lead to the Alkali-Silica Reaction (ASR) due to the reaction between alkali and silica in the pore solution. The reaction will cause the formation of the Alkali-Silica Gel (ASG). In the presence of moisture, the ASG will expand and finally cause cracking within the concrete structure.

Substituting part of the cement with Supplementary Cementitious Materials (SCM) has been found to be effective in controlling the ASR expansion within the mortar and concrete. Previous studies stated that the main mechanism of how SCM reduced the ASR expansion is by reducing the hydroxyl ion (OH<sup>-</sup>) in the pore solution (Kawamura and Takemoto, 1988; Thomas, 2011). Other mechanisms of ASR suppression are through alkali binding, improving the pozzolanic reactivity, limiting permeability and reducing the dissolution of silica (Shafaatian *et al.*, 2013). The effectiveness of SCM in

reducing the ASR expansion depends on several factors such as reactivity of aggregate, alkali content of cement and fineness of SCM (Rajabipour *et al.*, 2015; Afshinnia and Rangaraju, 2015).

Research on Palm Oil Fuel Ash (POFA) revealed that POFA is able to mitigate ASR damage. However, a higher amount of replacement was required in order to control the effect of ASR (Abdul-Awal and Hussin, 1997) but this has significantly reduced the strength of mortar produced (Tay and Show, 1995). Recent research on POFA showed that the effectiveness of POFA in controlling the ASR can be improved by reducing POFA into ultrafine size (Asrah *et al.*, 2015). However, the mechanism of how ultrafine POFA (UPOFA) controls the ASR has not yet being studied. Despite having high alkalis content than cement, POFA is still effective in suppressing the ASR expansion. Therefore, further research is required in order to improve the knowledge on the effect of UPOFA on ASR. This study reports on the mechanism of how

UPOFA controls the ASR expansion within the mortar bars. The effect of fineness and amount of UPOFA replacement on the pozzolanic reactivity, amount of CSH and effect on the silica dissolution are also discussed.

**MATERIALS AND METHODS**

Ordinary Portland Cement (OPC) used in this study has a specific gravity of 3.14 and BET 0.841 m<sup>2</sup>/g. The Palm Oil Fuel Ash (POFA) was collected from the Lumadan Palm Oil mill in Beaufort, Sabah, Malaysia. Prior grinding, POFA was dried in the oven at 105°C for 24 h. Subsequently, POFA was passed the 300 µm sieve and labeled as unground POFA (UG). POFA was then ground in the Los Angeles abrasion machine and planetary grinding mill to produce the ultrafine (UPOFA) and medium size POFA (MPOFA). UG POFA was used as a comparison. Reactive aggregate used in this research was collected from Penampang quarry, Kota Kinabalu, Sabah and identified as the sandstone aggregate. The aggregate was then crushed for the ASR testing in accordance to ASTM C1567. Table 1 and 2 show the chemical and physical properties of OPC and POFA used in this research.

To investigate the effect of UPOFA on the ASR expansion, further testing on pozzolanic reactivity was done. Mortar cubes 50×50×50 mm were cast and cured in saturated lime solution for 7 and 28 days. The strength activity index of mortar samples was determined according to ASTM C311 by crushing the mortar samples using the universal testing machine. The determination of the strength activity index was done by dividing the average compressive strength of POFA mortar with control mortar and expressed in percentage. In order to study the hydration product of mortar, Thermo Gravimetric (TGA) testing was performed. The preparation of samples was done by immersing the mortar cubes in acetone in order to stop the hydration. Consequently, the samples were crushed with a hammer and then ground to a finer size using the planetary grinding mill. The TGA measurements were done by using pyris 6 TGA at a heating rate of 20°C/min from 25°-700°C under continuous N<sub>2</sub> flux (20 mL/min).

The effect of aggregate dissolution due to the ASR was assessed by immersing soda lime glass in 340 mL of NaOH solution in the presence of 20 and 40% of POFA at 80°C and the reading on the weight of soda lime glasses was obtained at 7 and 14 days of testing. During the measurement, the glasses were removed from the NaOH solution and then washed thoroughly to remove any silica gel formed on the surface using distilled water. The weight of the glass was then recorded.

**Table 1: Chemical composition of OPC and POFA**

Chemical composition	OPC (%)	POFA (%)
Silicon dioxide (SiO <sub>2</sub> )	13.80	45.40
Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	3034	2.09
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	3.83	2.82
Calcium Oxide (CaO)	56.89	6.02
Magnesium oxide (MgO)	1.88	4.84
Sodium oxide (Na <sub>2</sub> O)	0.13	0.11
Potassium oxide (K <sub>2</sub> O)	1.08	7.07
Sulphur trioxide (SO <sub>3</sub> )	3.51	0.19
LOI	0.41	4.96
Na <sub>2</sub> O <sub>eq</sub>	0.84	4.76

**Table 2: Physical properties**

Materials properties	OPC	UPOFA	MPOFA
Median particle size (d <sub>50</sub> ) (µm)	4.000	1.230	17.39
BET surface area (m <sup>2</sup> /g)	0.841	3.666	3.651
DH desorption (m <sup>2</sup> /g)	2.950	8.263	5.051
Specific gravity	3.140	2.620	2.450

**RESULTS AND DISCUSSION**

**Mortar bar expansion:** The ASR expansion of mortar bars was evaluated according to ASTM C1567. The expansion of more than 0.2% at 14 days of NaOH exposure was considered as highly reactive and <0.1% as non-reactive. From Fig. 1, the Control Mortar (CM) samples show higher reactivity with the expansion of 0.289% at 14 days. The addition of UG POFA was unable to reduce the expansion of mortar bar for replacement below 30%. When MPOFA was used the effectiveness was improved to 30-40% of POFA replacement. Total 10-20% MPOFA replacement was insufficient to reduce the ASR expansion within the mortar bar. The effectiveness of POFA in controlling the ASR expansion was then further improved by using UPOFA. The replacement of OPC with 20-40% UPOFA in mortar has reduced the expansion to 0.098% (UF2), 0.045% (UF3) and 0.028% (UF4) which fell below 0.1% and was considered as non-reactive expansion. These results clearly reveal that the finer the particle size of POFA, the better their ability to suppress the ASR expansion. The effectiveness of UPOFA to suppress ASR might be due to the formation of more Calcium Silicate Hydrate (CSH) resulting from the improvement on the pozzolanic reactivity (Thomas, 2011; Kroehong *et al.*, 2011; Jain, 2012; Durand *et al.*, 1990). This indicates that the ability of POFA to suppress the ASR mainly depends on their fineness and level of replacement.

**Pozzolanic reactivity of UPOFA:** The pozzolanic reactivity of UPOFA was evaluated according to the Strength Activity Index (SAI) determined as in ASTM C 311 and the result is shown in Fig. 2. It can be clearly seen that all UPOFA samples show higher SAI at 7 and 28 days, indicating high pozzolanic reactivity due to its high fineness.

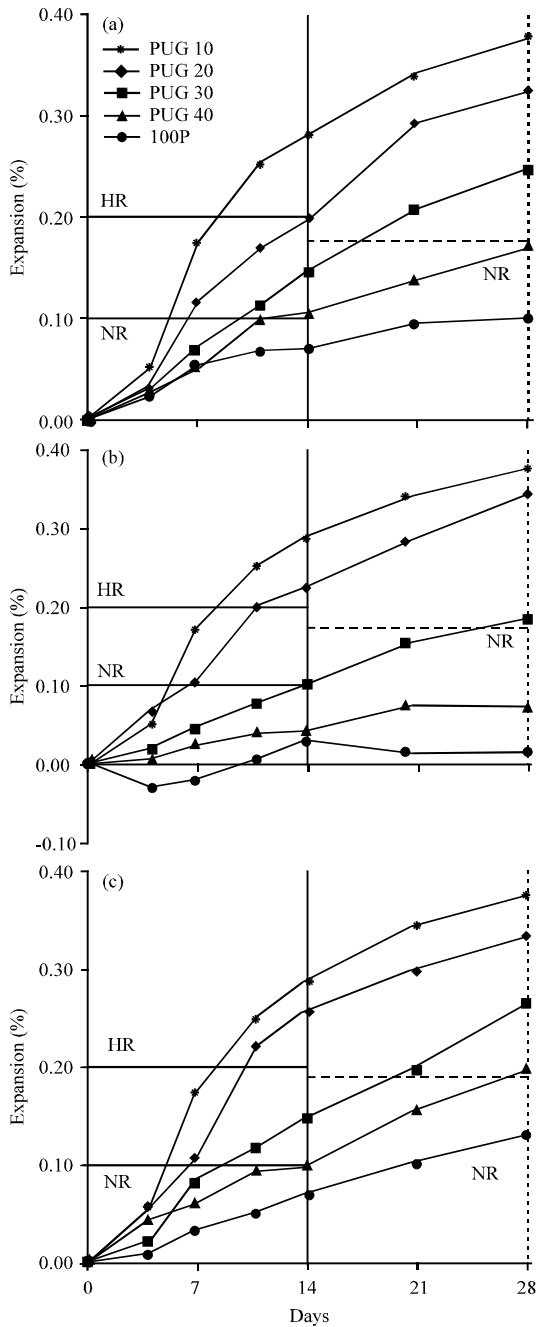


Fig. 1: ASR expansion of mortar bars containing: a) UG; b) UPOFA and c) MPOFA at 10-40% cement replacement

Even though UF4 showed slightly lower SAI as compared to CM, it still met the 75% limitation proposed by ASTM C618 (Kroehong *et al.*, 2011). In general, MPOFA exhibited lower SAI as compared to UPOFA especially at the early 7 days age but the SAI improved later on at the age of 28 days. The high fineness UFOFA has increased the pozzolanic reactivity

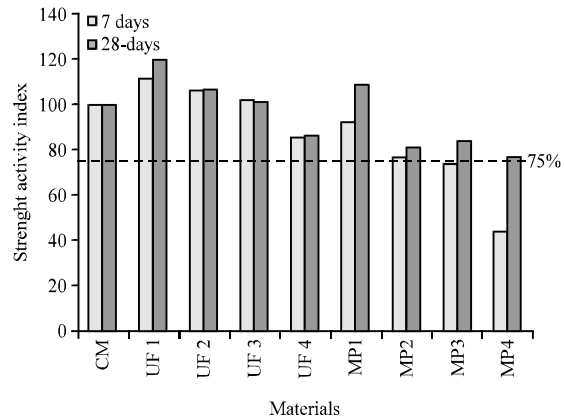


Fig. 2: Strength activity index of UPOFA and MPOFA mortars

of mortar and formed extra CSH which was responsible for the mechanical strength of the mortar produced. The addition of POFA also can improve the packing effect and change the pore structure to be more dense (Jain, 2012). On the other hand, the coarser size of POFA tends to slow down the process of hydration reaction mainly at the early age.

**Calcium Silicate Hydrate (CSH) and Calcium Hydroxide (CH) content:** To verify the effect of pozzolanic reactivity of UPOFA, TGA analysis was performed. The evaluation was done to determine the amount of hydration product of mortar containing 20 and 40% of UPOFA and MPOFA. The results are shown in Fig. 3. It can be seen that controlled mortar has high CH content for all ages of testing. When POFA was used to replace the cement, the amount of CH produced decreased. However, it can be seen that regardless of size, the high amount of CH was produced for POFA replacement at 20% as compared to 40%. The effect of pozzolanicity can be observed from the change of the CH amount of each sample as the age of testing increases. There were reductions in the amount of CH as the age of mortar matures. For example, the amount of CH for UF2 decreased from 0.847% (7 days) to 0.839 and 0.827% at 28 and 56 days, respectively. The reduction in the CH content indicates the consumption of CH to produce pozzolanic CSH in the mortar sample. The amount of CSH produced is shown in Fig. 3b.

From Fig. 30b, the high fineness of UPOFA has speed up the pozzolanic reaction of UF2 and UF4 samples, hence higher amount of CSH was produced particularly at a later age (28 and 56 days). The CSH gel produced was able to fill up pores within the mortar thus, a less permeability mortar was produced. This explains the effectiveness of UPOFA to suppress the ASR expansion even when a lower amount of UPOFA was used to replace the cement in the mortar bar.

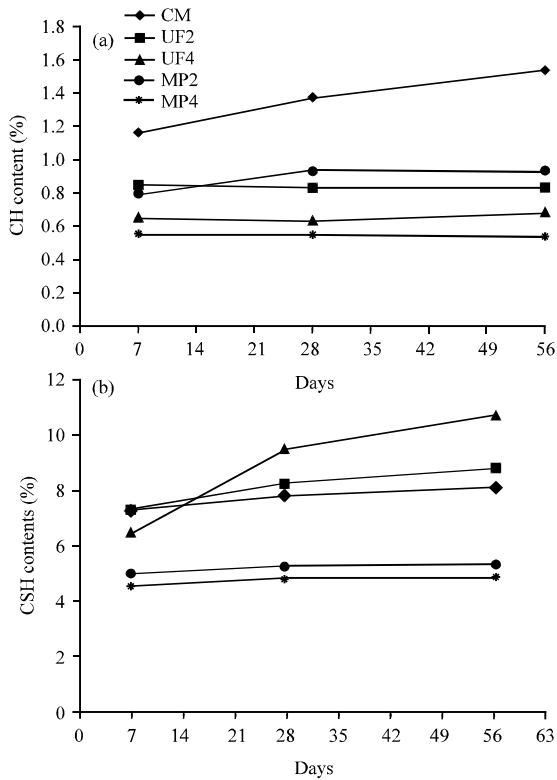


Fig. 3: a) Calcium Hydroxide (CH) content of mortars containing UPOFA and MPOFA and b) Calcium Silicate Hydrate (CSH) produced due to the pozzolanic reaction

As for MP2, despite having higher CH content, less amount of CSH was produced. This was due to its coarser size which has slowed down the pozzolanic reaction. Hence, it was unable to reduce the ASR expansion in the mortar bar as reported in study (Fig. 1b). For MP4, even though it has less amount of CSH, the ability to suppress the ASR expansion might be governed by the higher amount of POFA present in the mortar bar which has improved the ability of POFA to bind alkali in the pore solution. This phenomenon is discussed in detail.

**Aggregate dissolution:** Previous studies stated that the main mechanism of ASR reduction by pozzolana is through the reduction of alkali in the pore solution (Kawamura and Takemoto, 1988; Thomas, 2011; Jain, 2012; Ichikawa and Miura, 2007). High alkali ( $K^+Na^+$ ) will cause the release of more  $OH^-$  ion that will cause breakdown of silica from the reactive aggregate (Chappex and Scrivener, 2012). In order to assess the performance of UPOFA to reduce the ASR expansion, the effect of UPOFA on silica dissolution and  $OH^-$  concentration were investigated. This was done

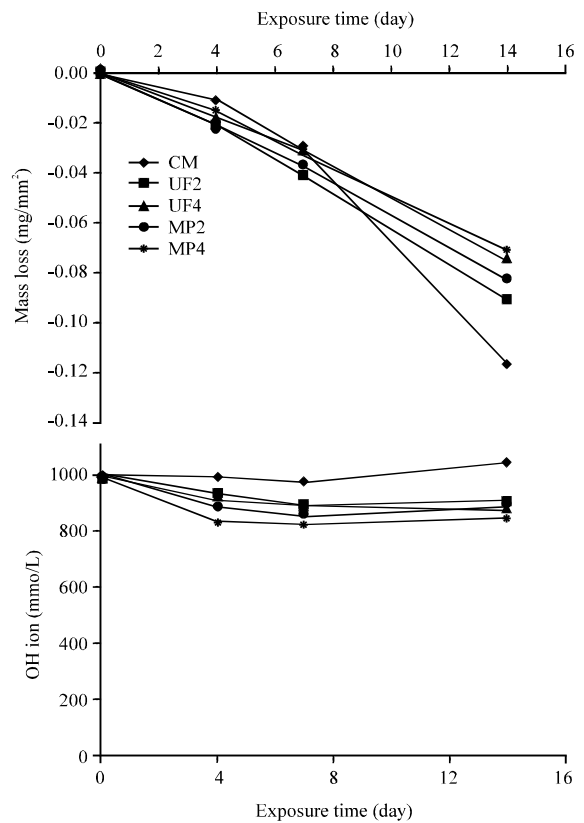


Fig. 4: a) The effect of POFA on the mass loss of soda lime glass and b) Hydroxyl ion ( $OH^-$ ) concentration in NaOH solution containing UPOFA and MPOFA.

through the measurement of mass loss of soda lime glass and titration of the NaOH solution (containing 20 and 40% POFA) at 4, 7 and 14 days of testing. The results are presented in Fig. 4 a-b. It was found that the mass loss of the soda lime glass increased as the age of testing increased due to the dissolution of silica content. At the early day of testing, the concentration of  $OH^-$  in control NaOH solution (without POFA) was high with 973 mmol/l. Later, not much change was observed on the  $OH^-$  concentration indicating the reaction between hydroxyl ion and silica was still high. Higher dissolution of silica resulted in the increased of mass loss of soda lime glass from 0.012% at day 4 to 0.117% at day 14. Meanwhile, the addition of UPOFA and MPOFA has reduced the  $OH^-$  concentration in NaOH solution (Fig. 3b) and led to the reduction on the dissolution of soda lime glass. However, the effect of POFA fineness to bind alkali was not very significant, since UPOFA and MPOFA showed almost similar reduction effect. The effect of fineness was more significant in improving the pozzolanic reactivity of POFA as discussed in the previous study.

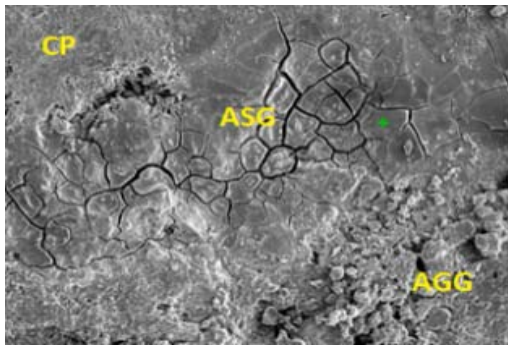


Fig. 5: Alkali-Silica Gel (ASG) formed along line between the aggregate and cement paste

Table 3: Alkali-silica gel composition in mortar bars at 14 days NaOH solution exposure

Variables	C	O	Na	Al	Si	K	Ca	C/S
100P	6.57	53.38	0.58	4.19	9.49	0.00	14.72	1.55
UF2	4.97	59.64	0.91	1.61	27.33	0.14	3.95	0.14
UF4	4.73	56.60	3.33	4.74	25.12	0.17	4.06	0.16
MP2	4.05	57.01	0.33	0.37	35.53	0.09	1.76	0.05
MP4	4.09	59.67	0.15	0.34	31.80	0.02	2.85	0.09

Nevertheless, the amount of replacement level seems to have an important effect in reducing the OH<sup>-</sup> and soda lime glass mass loss. UF4 and MP4 lowered the mass loss by 2.9-3.9% as compared to UF2 and MP2 with 1.1-2.32%. This indicates that higher level of replacement led to lower silica dissolution.

The mechanism of OH<sup>-</sup> reduction was believed due to the tendency of OH<sup>-</sup> to attack POFA rather than dissolving the silica from the glass (Shafaatian *et al.*, 2013). OH<sup>-</sup> binds alkalis from POFA; therefore, the concentration of alkalis was lowered. The higher the amount of UPOFA or MPOFA used, more OH<sup>-</sup> was bound to the alkalis therefore, less ASR expansion was observed for mortar bars containing a high level of POFA as cement replacement.

**Chemical composition of alkali silica gel:** Determination of the alkali-silica gel was done on mortar samples containing 20 and 40% of UPOFA and MPOFA replacement which were immersed in an alkali solution for 14 days. Cracks due to ASG were observed along the aggregates voids and near cracks (Fig. 5). The result of the chemical composition of ASG is shown in Table 3.

It was observed that controlled mortar (100 P) has higher calcium content (14.72%) but lower in potassium content (0%) as compared to 20 and 40% UPOFA (UF2 and UF4). The increase of Ca<sup>+</sup> due to the release of OH<sup>-</sup> has increased the Ca<sup>+</sup> in the pore solution of the

controlled mortar. The ability of Ca<sup>+</sup> to replace alkali in the ASG has led to the formation of rich calcium ASG (Durand *et al.*, 1990). Meanwhile, replacing cement with UPOFA has reduced the Ca<sup>+</sup> content in the ASG. Therefore, the ASG formed in UF2 and UF4 was rich in alkali but low in Ca<sup>+</sup> with 3.95 and 4.06%, respectively. Low Ca<sup>+</sup> ASG is characterized with a less viscous gel that causes less or no expansion while high Ca<sup>+</sup> usually has hard and viscous gels which lead to high expansion (Kim *et al.*, 2015).

The phenomenon of low Ca<sup>+</sup> content in ASG of UPOFA mortars can be related to the pozzolanic reactivity of UPOFA. In the previous study, it was explained that high pozzolanic reactivity of UPOFA leads to a reduction in the CH consumption due to the formation of extra CSH. This additional CSH is able to bind the alkalis within the pore solution. Therefore, lower OH<sup>-</sup> is produced. Lower OH<sup>-</sup> concentration will reduce the breakdown of silica from the reactive aggregates. Therefore, less expansion was observed. On the other hand, the consumption of CH to produce CSH also will lower the Ca<sup>+</sup> in the pore solution therefore, not much Ca<sup>+</sup> is available for the formation of ASG and this explains the lower Ca<sup>+</sup> amount in the ASG of mortar containing UPOFA.

## CONCLUSION

- The main mechanism of POFA controlling ASR is by binding the alkali and reducing the OH<sup>-</sup> concentration. This has reduced the breakdown of silica from the reactive aggregate and ASR expansion within mortar bar
- The level of OPC replacement is an important factor in controlling ASR. The high amount of POFA replacement is required to give a good binding alkali effect
- The high fineness of UPOFA has improved the effectiveness to reduce the ASR expansion through improvement on the pozzolanic reactivity. Formation of extra CSH was able to fill pores within mortar and improve permeability of mortar
- The fineness of POFA has less effect on the alkali binding capacity in the aggregate dissolution test. Regardless of size, the effect of POFA in reducing silica dissolution was influenced by the amount of OPC replacement
- The use of UPOFA as cement replacement has changed the chemical composition of ASG formed due to ASR. ASG in the POFA mortar was rich in alkali but low in Ca<sup>+</sup> and this has produced a less viscous and expansive gel within the mortar samples

## ACKNOWLEDGEMENTS

Researchers would like to acknowledge the financial support from the Higher Ministry of Education of Malaysian government under the Fundamental Research Grant Scheme (FRGS), Grant No. FRG 0364-TK-1-2014.

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