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RESEARCH ARTICLE - CIVIL ENGINEERING

Effects of Binary and Ternary Blended Cements Made from Palm Oil Fuel Ash and Rice Husk Ash on Alkali–Silica Reaction of Mortar

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Abstract Alkali–silica reaction (ASR) of binary and ternary blended cement mortars made from fine particles of palm oil fuel ash (PA) and rice husk ash (RA) was investigated. Portland cement type I was replaced by PA, RA, and RA mixed with PA at rates of 10, 20, 30, and 40% by weight of binder and was used for casting mortar to investigate compressive strength and expansion due to ASR. After finishing ASR test, microstructures of the mortars due to ASR were also investigated by scanning electron microscope and energy-dispersive X-ray spectrometer. The results showed that PA and RA are good pozzolans considering in terms of compressive strength. For ASR results, the expansions of PA mortars due to ASR were lower than control mortar, while the mortars containing RA had very high expansion and many cracks. However, RA–PA mortars provided lower expansion due to ASR than RA mortars at the same rates.

Keywords Alkali–silica reaction · Palm oil fuel ash · Microstructure · Mortar · Rice husk ash · Ternary blended cement

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1 Introduction

Palm oil is one of agricultural products of oilseed. In 2015/16, United States Department of Agriculture (USDA) [1] reported that the palm oil production in the world was approximately 65 million metric tons, from which the major of this production crop was from Indonesia and Malaysia accounted for more than 90% of global. In addition, Thailand is the 3rd rank of palm oil production in the world or has the production approximately of 2.1 million tons from palm oil tree of 11 million tons. Moreover, palm oil production in Thailand has been trending upward approximately 22%, which is the first ranking of growth rate in the world. The palm oil fruits are pressed; they are separated from the press cake, which is almost an ample amount of approximately 70% by weight and to be changed into by-products as empty fruit bunches, fibers, and shells [2]. These by-products can be utilized by using fuel to generate electricity in the palm oil industry, and then it is turned into palm oil fuel ash (PA). PA is a truly waste of the industry, while Thailand has amount of PA approximately 300,000 tons per year and tends to increase sharply in the near future. The use of PA is little, while the major is sent to landfills causing dust since the small particles of PA can be easily spread. Although PA can be used to partially replace cement to produce concrete, the major utilization is still at the research in a laboratory.

PA was currently proved to be a good pozzolanic material for concrete. In 2003, Tangchirapat et al. [3], who early studied the properties of mortar containing PA, found that PA provided longer setting times of paste and needed more water requirement than control mortar while the use of 10% ground PA provided compressive strength of mortar higher than the control mortar of 2–4%. In term of durability, ground PA concrete had expansion due to magnesium sulfate attack less than concrete without ground PA [4] and concrete with

10–20% of small particles of PA by weight of binder had higher resistance of loss in compressive strength due to 5% $MgSO_4$ solution than concrete made from Portland cement types 1 and 5 [5]. In addition, ground PA could provide low drying shrinkage, low water permeability [6] and increase resistant of chloride diffusion [7].

Rice is the top rank in the world for raw major produced cereal, while Asian countries popularly consume rice as a main food. The statistic from 2015/16 by USDA [8] reported that the world has milled paddy approximately 710 million tons and is turned into milled rice approximately 480 million tons. Of course, the major production has come from China and India. Thailand is the 6th rank in the world by an amount approximately 25 and 16 million tons of paddy and milled rice production, respectively. After the process of cultivation, the remained residue such as straw and husk is left. Ratio between rice straw and paddy stayed at range of 1.0–4.3% and rice husk accounted for approximately 22% by weight of paddy [9]. Rice husk is a good fuel for boiler combustion with steam turbines to generate heat and electricity. After the last process of burning rice husk, rice husk ash (RA) is the residue. In Thailand, it is estimated that RA has been amount approximately 1.1 million tons per year. RA is slightly benefited such as it is used as a fertilizer to rebalance an agricultural soil while the major amount of RA is sent to landfills and has negative effect to environment similarly to PA. However, the use of RA in concrete mixture in Thailand is still at testing process similar to PA.

The use of RA in concrete was studied by Zhang and Malhotra [10] who used RA to produce high-performance concrete (HPC) and investigated concrete in fresh states such as workability, segregation, setting time, and hardened states such as compressive strength, spitting tensile strength, flexural strength, modulus of elastic, drying shrinkage, penetration of chloride, and freezing-thawing. The results demonstrated that RA could be used as a pozzolan and could also be used in HPC [11].

Alkali–silica reaction (ASR) is a reaction between alkalis in cement or binder and reactive silica in aggregate and changes the product to be calcium–alkali–silicate–hydrate gel or short name “ASR gel” and the gel can swell by absorbing water or moisture, expand and produce pressure around aggregate to cement paste [12]. Many researchers reported that the partial replacement of OPC by pozzolans could solve ASR problem such as the use of 40% fly ash class F, 65% slag, 15% condensed silica fume [13], and 30% fly ash class C [14]. The study of PA on ASR had been investigated long ago in 1997 by Awal and Hussin [15], who used PA with 2.7% alkali content ($Na_2O + 0.658K_2O$) to replace cement at rates of 10, 30, and 50% by weight of binder and found that the mortar containing PA had expansion due to ASR lower than the mortar without PA. Moreover, the replacing 50% PA provided the expansion lower than 0.10% at 14 days. However, the replacing of OPC by 50% PA may produce low compressive strength.

Zerbino et al. [16] studied the effect of natural and ground RA on ASR and presented that the natural RA mortar had expansion due to ASR more than control mortar about 4 times, while ground RA mortar had expansion due to ASR lower than control mortar. This result suggested that the use of pozzolan to replace OPC may or may not be efficient to reduce the expansion due to ASR of mortar. A study of ternary blended cement on ASR was studied by Moser et al. [17], who found that the expansions due to ASR of mortars containing metakaolin mixed with fly ash were lower than only fly ash mortar. In addition, they also found that the replacement of 8% metakaolin and 25% fly ash had the expansion due to ASR lower than the use of 8 and 15% of metakaolin in mortars.

RA has been proved to be a good pozzolan, however, it may not be a good pozzolan to reduce ASR. The use of RA to replace OPC may not be sufficient to control the expansion due to ASR, so this research studied the use of PA, RA, and RA mixed with PA as pozzolanic materials to replace OPC. Compressive strengths and expansions due to ASR of mortars containing PA, RA, and RA mixed with PA were presented. Moreover, the surfaces of mortars, crack characteristic, SEM, and EDS of mortars after finishing of ASR testing were also investigated.

2 Experimental Program

2.1 Materials

2.1.1 Cement

Ordinary Portland cement (OPC) with a low alkali content (0.56% of Na_2O_{eq}) was used as a primary binder material (Table 1).

2.1.2 Palm Oil Fuel Ash

Palm oil fuel ash (PA) was obtained from palm oil industry in Samut Sakhon province, Thailand. PA was directly obtained from the industry at dry state. As it has a large amount of particles retained on a No. 325 sieve (42.1% by weight), it was ground by a ball mill to improve its pozzolanic activity. After grinding, the retained on a No. 325 sieve was 5.2% by weight; the fine particles of palm oil fuel ash (assigned as PA) had a specific gravity of 2.40.

PA mineral composition was investigated by the X-ray diffraction (XRD) analysis, and the result is given in Fig. 1. The XRD of PA shows the clear peak of sylvite synonym potassium chloride (syn—KCl) in the cubic form, quartz silicon dioxide (SiO_2) in the form of hexagonal, and arcan-

Table 1 Chemical compositions of Portland cement type I, ground palm oil fuel ash (PA) and ground rice husk ash (RA), and reactive aggregate

Chemical composition (%)	Portland cement type I	PA	RA	Reactive aggregate
SiO_2	20.9	47.1	86.3	5.5
Al_2O_3	4.8	1.0	0.2	0.5
Fe_2O_3	3.4	2.5	0.4	0.5
CaO	65.4	13.3	0.8	91.3
SO_3	2.7	6.3	0.2	0.1
MgO	1.3	4.6	0.4	1.7
Na_2O	0.3	0.6	–	–
K_2O	0.4	20.0	3.0	0.1
Loss on ignition (LOI)	1.0	4.3	8.7	–
Summation	100.2	99.7	100.0	99.7
$Na_2O_{eq} = Na_2O + 0.658K_2O$	0.56	13.76	1.97	–

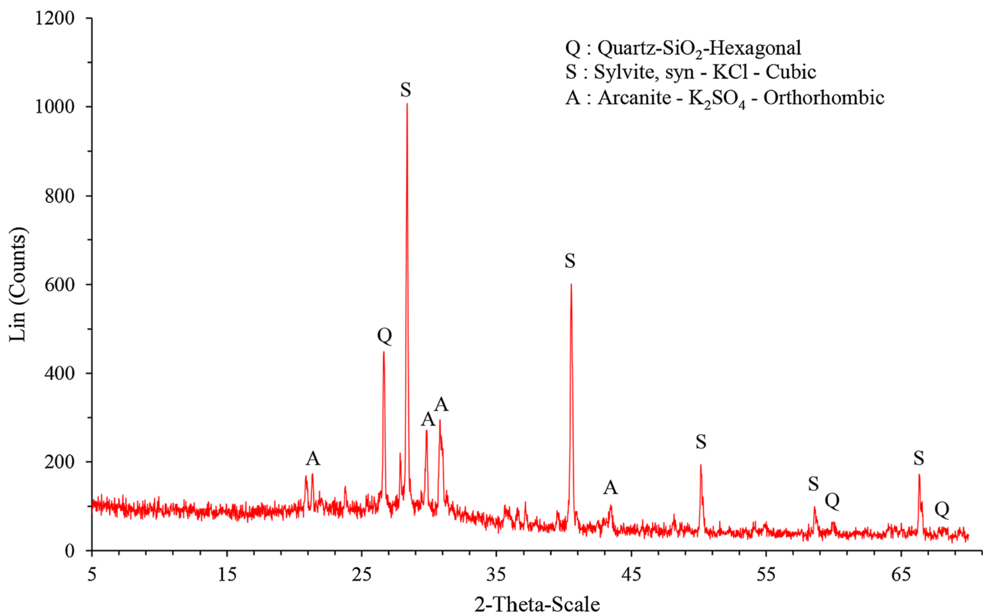


Fig. 1 X-ray diffraction (XRD) of PA

ite potassium sulfate (K_2SO_4) of orthorhombic. Sylvite is a raw material for producing the potassium fertilizes such as fertilizes of potassium chloride and potassium sulfate. The above-mentioned XRD of PA demonstrated that PA contained many fertilize compounds and remained in PA.

Table 1 presents the chemical compositions of PA and RA carried out by X-ray fluorescence spectrometer analysis (XRF). PA has the amount of $SiO_2 + Al_2O_3 + Fe_2O_3$ (below 70%) and a high amount of alkali (20.0% of K_2O, and 13.3% of CaO). Its high sulfur trioxide (SO_3) content (6.3%) may promote the internal sulfate attack of the binder as a result of ettringite formation. ASTM C618 [18] specified SO_3 to be lower than 4% for class N pozzolan and 5% for fly ash (class C or class F). The loss on ignition (LOI) of PA (4.3%) was lower than the maximum value specified by ASTM C618 [18] for pozzolan class N and fly ash (class C or class F).

One important component for ASR is the alkaline in a pozzolan from which PA in this study has alkali contents ($Na_2O_{eq} = Na_2O + 0.658K_2O$) of 13.76% by weight. In addition, PA from the previous studies demonstrated that PA with summation of major compositions ($SiO_2 + Al_2O_3 + Fe_2O_3$) of less than 70% could be used as a good pozzolan [4,19,20]. Moreover, Awal and Hussin [15], who investigated the expansion due to ASR of mortar containing PA with low major compositions (59.7%), found that the PA provided expansion due to ASR of mortar lower than control mortar.

2.1.3 Rice Husk Ash

Rice husk ash was collected from a rice mill industry in Lopburi province, Thailand. Since the received rice husk ash had a high amount of material retained on a No. 325 sieve

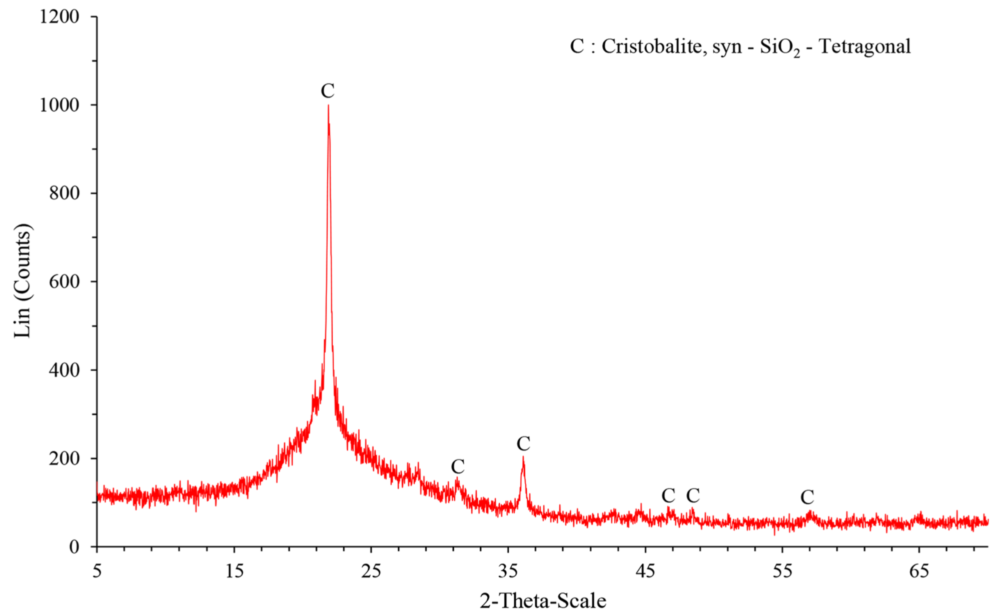


Fig. 2 X-ray diffraction (XRD) of RA

(77.6%), it was ground to improve its pozzolanicity. After grinding (the retained on a No. 325 sieve was 4.2%), RA had a specific gravity of 2.31.

The XRD results of RA is presented in Fig. 2, which shows a clear peak only of cristobalite SiO_2 in crystal system of tetragonal. Normally, the stability cristobalite SiO_2 is occurred only above at temperature of 1470 °C [21], while the cristobalite SiO_2 of RA in this study received from burning rice husk at temperature of 950 °C; thus, RA has unstable cristobalite SiO_2 or quickly reactive SiO_2. For chemical compositions, RA has a major composition of SiO_2 of 86.3% by weight, while Al_2O_3 and Fe_2O_3 are less than 1% by weight. SO_3 of RA is also very low at 0.2% by weight, while the value of LOI is 8.7% by weight. Moreover, RA has Na_2O_{eq} of 1.97% by weight.

2.1.4 Fine Aggregate and Reactive Aggregate

River sand was used as a fine aggregate for testing strength activity index of mortar. For ASR testing, a reactive coarse aggregate from Saraburi province (Central of Thailand) was used in this investigation. It was crushed and used as a fine reactive aggregate. Table 2 shows the grading requirements for the fine reactive aggregate by ASTM C1260 [22]. The crushed stone with this grading has a specific gravity (SSD) of 2.63. Physical properties of reactive aggregate were investigated such as color, powder color, crystalline, crack, and luster. The results showed that the reactive aggregate is a limestone with a high calcite ($CaCO_3$) content and minor amounts of quartz and dolomite, according to the XRD analysis shown in Fig. 3. In addition, major oxide of reactive aggregate was CaO (91.3%) and minor oxides were SiO_2 and MgO (see Table 1).

Table 2 Grading requirement of crushed aggregate to be used as fine aggregate for ASR testing

Sieve size		Mass (%)
Passing	Retained on	
4.75 mm	2.36 mm	10
2.36 mm	1.18 mm	25
1.18 mm	600 µm	25
600 µm	300 µm	25
300 µm	150 µm	15

2.1.5 Water and Solution

Tap water was used in process of casting and curing of mortars. Distilled water was used to produce 1 N of sodium hydroxide solution (NaOH commercial grade) from which NaOH 40 g was dissolved in distilled water 900 mL and filled distilled water to obtain a solution of 1.0 L.

2.2 Mixture Proportion and Testing for Strength Activity Index

Strength activity indices (SAIs) of mortars were investigated by using pozzolanic materials (PA, RA, or PA mixed with RA) to replace OPC at a rate of 20% by weight of binder, while the control mortar (CT mortar) was made from 100% OPC as a binder. River sand was used as a fine aggregate

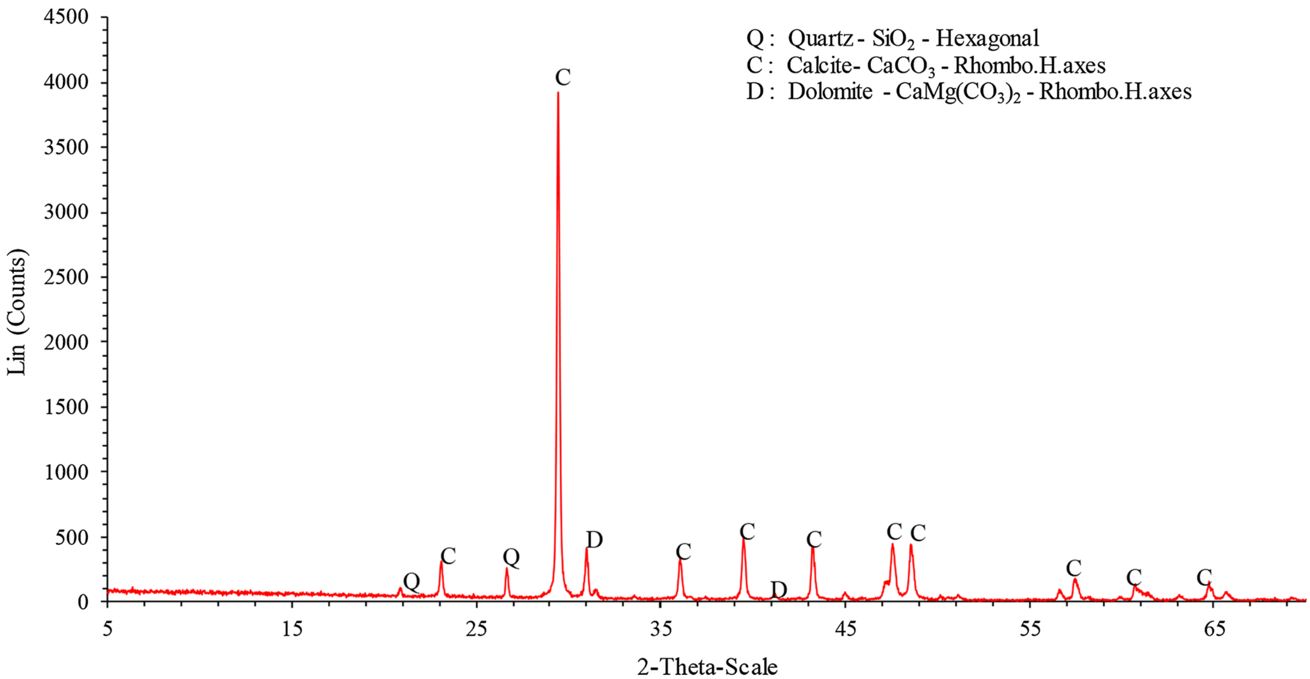


Fig. 3 X-ray diffraction (XRD) of reactive aggregate

with a ratio of cement or binder to fine aggregate of 1:2.75 by weight to cast mortars. Water to binder (W/B) ratios of mortars were adjusted to produce flows of 110 ± 5% according to ASTM C1437 [23].

SAI was obtained from the compressive strength of mortar which was investigated according to ASTM C109 [24]. Each mix proportion used five mortar cube specimens with dimensions of $50 \times 50 \times 50\,\text{mm}^3$, and the mortars were tested to determine the compressive strength at ages of 7 and 28 days, as indicated by ASTM C618 [18]. SAI was calculated by Eq. (1) [25], from which the compressive strengths of mortars containing PA, RA, or PA mixed with RA were compared with CT mortar.

$$\%\ \text{SAI} = \frac{A}{B} \times 100 \tag{1}$$

where A is the average compressive strength of mortar containing PA or RA or PA mixed with RA (MPa) and B is the average compressive strength of CT mortar (MPa).

2.3 Mixture Proportion and Testing for ASR

Mix proportion of mortars for ASR test are shown in Table 3. The mortar contained 1 part of binder and 2.25 parts of fine reactive aggregate. The water to binder (W/B) ratio was set as a constant of 0.47 according to ASTM C1260 [22]. The binder of mortars, both binary blended cements (PA or RA) and ternary blended cement (PA + RA), was used to replace OPC at rates of 10, 20, 30, and 40% by weight of binder.

A mortar bar with dimensions of $285 \times 25 \times 25\,\text{mm}^3$ was used to investigate expansion due to ASR in accordance with ASTM C1260 [22]. After casting 24 h, the mortar bars were removed from the molds and cured in water at a temperature of 80 °C for 24 h and then zero reading length of the mortar bars was measured. After the zero reading length, the mortar bars were immersed at 1 N of NaOH solution with the volume 4 times of the specimens. Length change of mortar bars were measured until 28 days of immersion in 1 N of NaOH solution. The length change of mortar bars were calculated as suggested by ASTM C490 [26].

3 Results and Discussion

3.1 Strength Activity Index

Table 4 shows the compressive strengths and the strength activity index (SAI) of mortars containing PA, RA, and RA mixed with PA at rate of 20% by weight of binder. SAI of mortar is a pozzolanicity that is used to measure how good a pozzolan is. ASTM C618 [18] defines that a good pozzolan should have SAI more than 75% at the ages of 7 or 28 days. In this study, CT mortar had the compressive strengths of 22.8 and 28.3 MPa at the ages of 7 and 28 days, respectively.

PA mortar (containing PA at 20% by weight of binder) had 7- and 28-day compressive strengths of 18.2 and 25.7

Table 3 Mix proportions of mortars

Mixes	Mix proportions (by weight)				
	Cement	PA	RA	Fine aggregate	W/B
For Strength Activity Index testing					
CT	1.00	–	–	2.75	0.67
PA20	0.80	0.20	–		0.67
RA20	0.80	–	0.20		0.72
RA10PA10	0.80	0.10	0.10		0.70
For alkali–silica reaction testing					
CT	1.00	–	–	2.25	0.47
PA10	0.90	0.10	–	2.25	0.47
PA20	0.80	0.20	–		
PA30	0.70	0.30	–		
PA40	0.60	0.40	–		
RA10	0.90	–	0.10	2.25	0.47
RA20	0.80	–	0.20		
RA30	0.70	–	0.30		
RA40	0.60	–	0.40		
RA5PA5	0.90	0.05	0.05	2.25	0.47
RA10PA10	0.80	0.10	0.10		
RA15PA15	0.70	0.15	0.15		
RA20PA20	0.60	0.20	0.20		

Table 4 Compressive strength and strength activity index (SAI) of mortar

Sample	CT	PA	RA	RA mixed with PA
Compressive strength (MPa)				
At 7 days	22.8	18.2	18.0	19.7
At 28 days	28.3	25.7	26.9	26.2
Strength Activity Index (%)				
At 7 days	100	83	79	87
At 28 days	100	87	91	89

MPa (SAI of 83 and 87%), respectively, suggesting a good pozzolan, although the chemical compositions of PA were not met the requirement of ASTM C618 [18]. The results also suggested that the chemical compositions specified by ASTM C618 [18] are not a sole parameter to indicate the pozzolanic activity of PA since the standard is the specification for coal fly ash and raw or calcined natural pozzolan.

RA mortar provided the compressive strengths of 18.0 and 26.9 MPa at the ages of 7 and 28 days, respectively, and had SAI higher than 75% both at 7 and 28 days which guaranteed the effectiveness of a good pozzolan for RA in terms of the compressive strength.

RA mixed with PA mortar (containing RA at 10% and PA at 10%) had the compressive strength more than both PA and RA mortars at the age of 7 days or had SAI of 87% and increased to 26.2 MPa or had SAI of 89% at 28 days. These results also suggested that RA mixed with PA is a good pozzolan to be used in concrete when the compressive strength is considered.

3.2 Expansion of Mortar Due to Alkali–Silica Reaction

3.2.1 Expansion of CT Mortar

The expansions due to ASR of CT mortar, as shown in Fig. 4, are 0.24 and 0.38% at 14 and 28 days, respectively. In this test method, the alkali content of the cement had little or no effect on mortar expansions. According to ASTM C1778 [27], the aggregate could be classified as moderately reactive since the mortar expansion due to ASR was between 0.10 and 0.30% at 14 days. Figure 5 shows the surface of CT mortar after immersion in 1 N NaOH solution at a period of 28 days while the enlarged figure shows small cracks of CT mortar with the width of less than 0.1 mm.

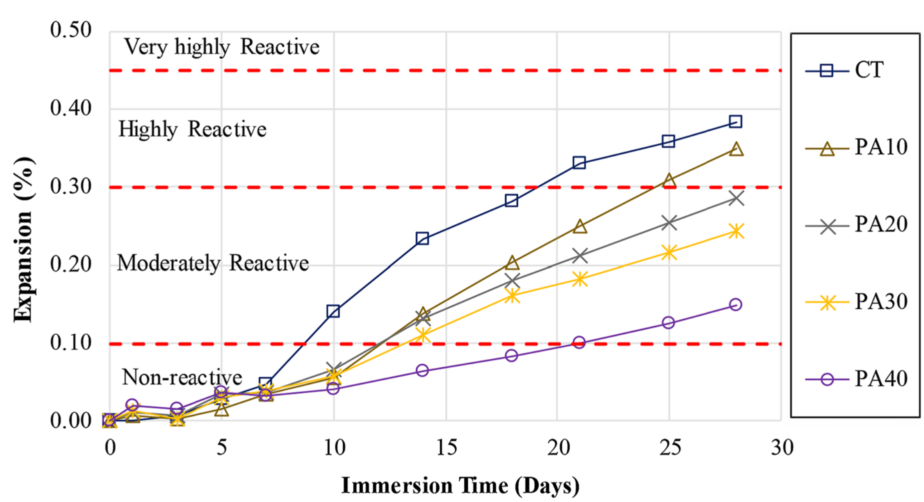


Fig. 4 Relationship between expansion of PA mortars due to ASR and immersion time

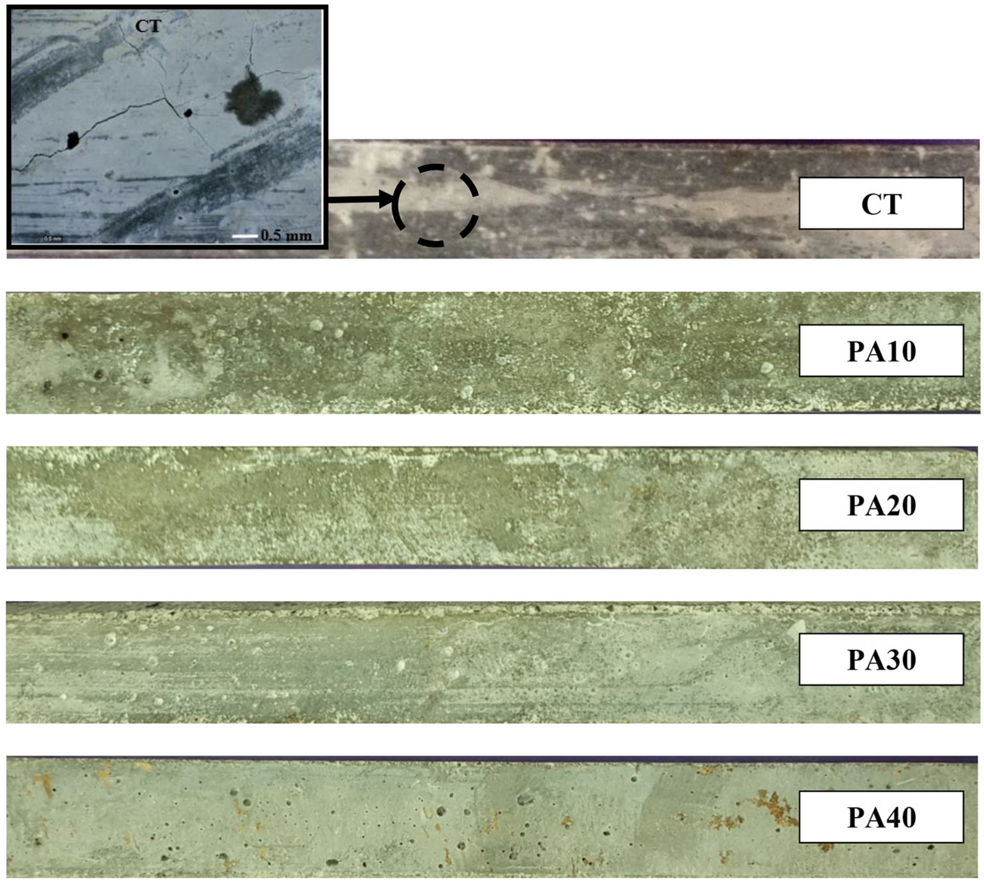


Fig. 5 Surfaces of CT and PA mortars after 28 days of immersion in 1 N NaOH solution

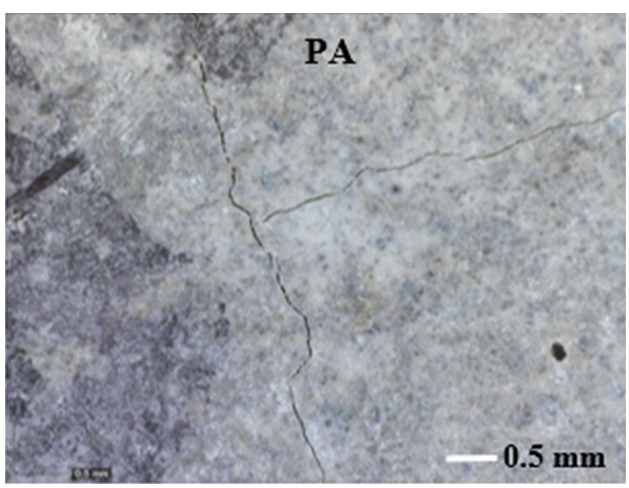


Fig. 6 Enlargement of the surface of PA10 mortar after 28 days of immersion in 1 N NaOH solution

3.2.2 Expansion of PA Mortars

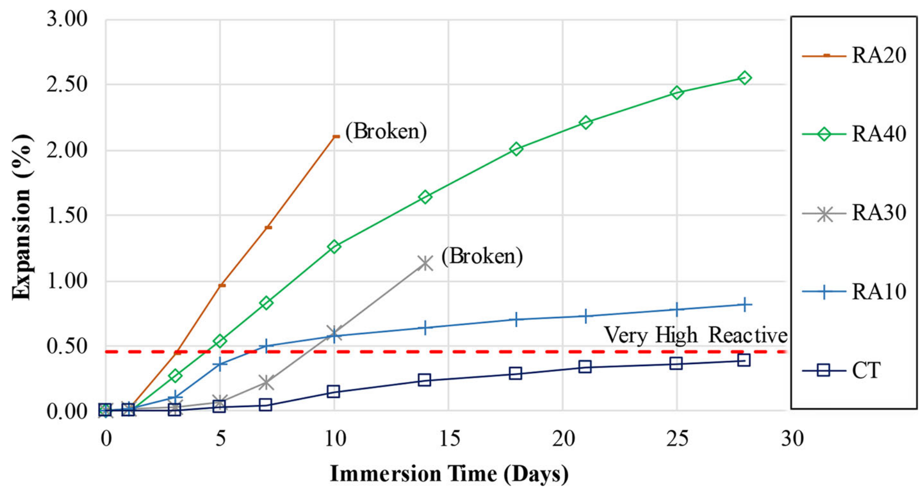
The expansions due to ASR of PA mortars are also presented in Fig. 4. It should be noted that PA can reduce the expansion of mortar due to ASR. This can be attributed to the replacement of OPC by PA caused reduction of CaO content and lowering $Ca(OH)_2$ content from pozzolanic reaction of SiO_2 and Al_2O_3 in PA. Both CaO and $Ca(OH)_2$ were the major components of calcium which could be dissolved to react with silica gel and produced the expansion of mortar [28]. Moreover, small particles of PA could fill pores in paste and pozzolanic reaction of PA could produce C–S–H and C–A–H to make mortar more dense [29]. These results show that the higher is the replacement of OPC by PA, the lesser is the expansion due to ASR. Despite its high alkali content, it seems PA is efficient to reduce the expansion of mortar bars due to ASR. However, it is important to recall that the accelerated mortar bar tests (AMBT) by ASTM C1260 [22] may not be appropriate for evaluating the effectiveness of the mineral admixtures to counteract the ASR.

The use of 40% replacement of PA could control the expansion due to ASR since the expansion of PA40 mortar was less than 0.10% at 14 days. These results were similar to Awal and Hussin [15], who found that the replacement of OPC by 50% of PA could reduce the expansion of mortar due to ASR below 0.10% at 14 days.

Comparing the use of PA and other pozzolans from many researchers, it was found that the use of 6 and 10% of silica fume by weight of binder provided the expansions of mortars near the use of PA in this study at rates of 30 and 40% by weight of binder, respectively [30]. In addition, the use of silica fume with low silica content (68.21%) at 4–12% of binder could not reduce expansion due to ASR of mortar to be lower than 0.10% at 14 days while mortars containing 8 and 12% of silica fume with normal silica content (88.40%) had the expansions lower than 0.10% at 14 days [31]. Moreover, the replacement OPC by a good pozzolan may not help to reduce the expansions due to ASR to be lower than 0.10% at 14 days if the control mortar had the high expansion and the replacement of the pozzolan was not high enough. For example, the use of 10–20% of fly ash and 1% of lithium carbonate by weight of binder replaced OPC could not reduce expansion due to ASR to be lower than 0.10% at 14 days since the control mortars had the expansions approximately of 0.35–0.83% [32]. Increasing amount of lithium carbonate to 2% by weight of binder provide the expansions of mortar lower than 0.10% at 14 days [32,33]. In addition, replacing OPC by 40% of PA provided the expansions similarly to the use of 15–25% of fly ash class F and 25–35% of fly ash class C [34].

Figure 5 shows the surfaces of PA mortars after they were tested for ASR at 28 days. PA mortars did not show any crack on the mortar surface by visual inspection. However, Fig. 6 shows small cracks of less than 0.1 mm in width from PA10 mortar since it is the mortar that had the highest expansion due to ASR.

Fig. 7 Relationship between expansion of RA mortars due to ASR and immersion time



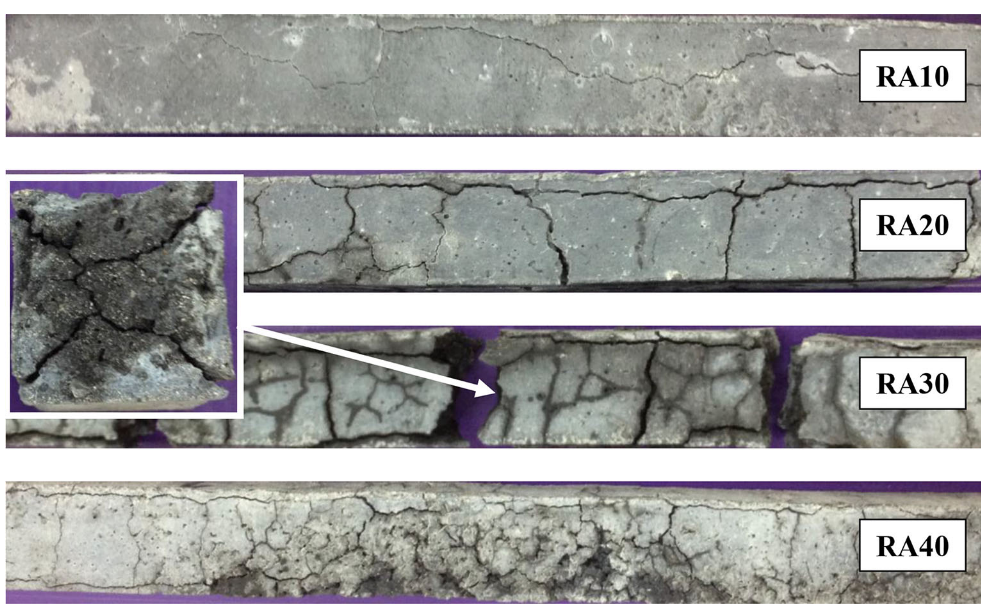
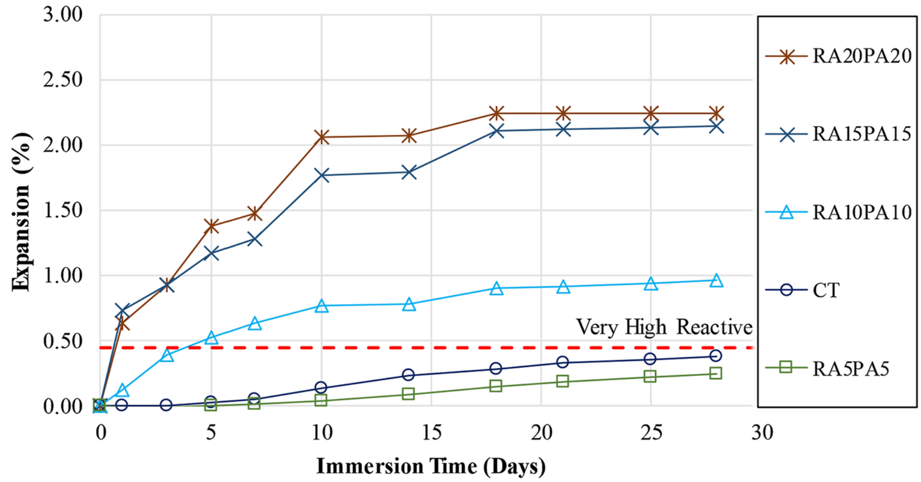


Fig. 8 Surfaces of RA mortars after 28 days of immersion in 1 N NaOH solution

Fig. 9 Relationship between expansion of RA mixed with PA mortars due to ASR and immersion time



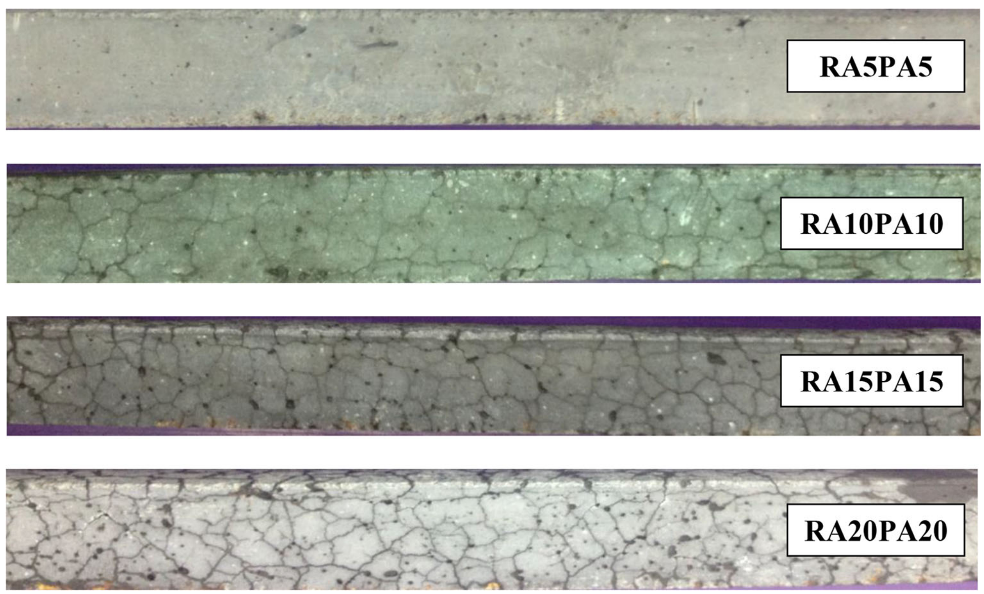


Fig. 10 Surfaces of RA mixed with PA mortars after 28 days of immersion in 1 N NaOH solution

3.2.3 Expansion of RA Mortars

The expansions due to ASR of CT and RA mortars are given in Fig. 7. All RA mortars had expansions greater than CT mortar.

RA20 mortar had the expansion due to ASR at 10 days of 2.102%, and then at 14 days, the three specimens of this mixture were broken, while RA30 mortar provided the last value of expansion due to ASR at 14 days of 1.137% before they were broken. The above results suggested that RA is a highly reactive material due to ASR because RA had high amount of unstable SiO_2 content. When RA mortar immersed in 1 N NaOH solution, unstable SiO_2 was easily activated at temperature of 80 °C; thus, the reaction between alkali in cement and SiO_2 in RA or in the aggregate caused mortar to have high expansion. It should be noted that the highly reactive SiO_2 in RA produced expansion due to ASR more than highly reactive SiO_2 in the fine aggregate. However, the high expansion due to ASR of RA mortar caused by the reactive of the coarse particles of cristobalite (retained on the No. 325 sieve) was observed by Zerbino et al. [16] who studied unground and ground RA and found that the use of unground RA affected to high expansion due to ASR of mortar, while the use of 15% of ground RA could reduce expansion due to ASR of mortar lower than 0.10% at 16 days. When they increased the replacement of ground RA to 25% by weight of binder, the expansions of mortar were increased. Furthermore, the self-compacting high performance (SCHP) concrete made from RA with crystalize structure of quartz; the low expansion due to ASR of SCHP concrete was obtained from the use of RA

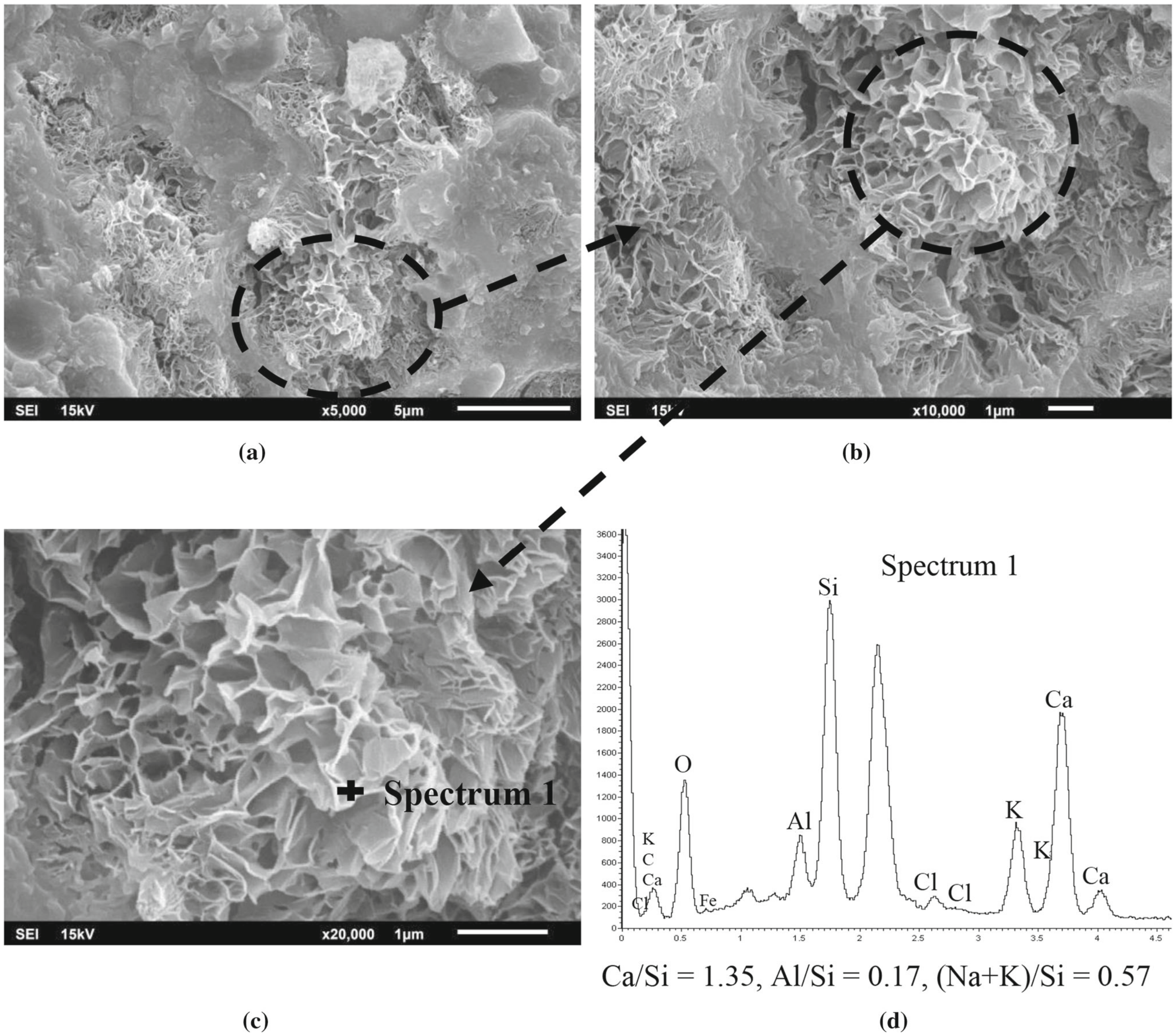


Fig. 11 SEM and EDS of PA10 mortar after 28 days of immersion in 1 N NaOH solution

with high fineness (median particle size of 5.7 micron) and the replacements of OPC by RA from 10 to 30% by weight of binder provided the expansions lower than 0.10% at 14 days [35].

The picture of RA mortars surfaces is given in Fig. 8, and it is easily seen that all mortars containing RA had many cracks. RA10 mortar had cracks along the longitudinal of mortar. Mortars RA20 and RA30 had widely cracks both longitudinal and horizontal directions due to very high ASR expansion. The lowest figure showed the map cracks of RA40 mortar surfaces. The results of this study also suggested that RA may not be effective to reduce the ASR of mortar. Test should be performed to confirm that the pozzolan could be used to improve compressive strength and ASR or other properties of the mortar or concrete.

3.2.4 Expansion of PA Mixed with RA Mortars

From the previous results, PA can be used to reduce the expansion of mortar due to ASR, but RA increases the expansion of mortar due to ASR; thus, RA is mixed with PA for the intension to reduce the high expansion due to ASR. The use of ternary blended cement for ASR in this study followed the findings of Esteves et al. [36], who found that the use of only fly ash could not reduce the expansions due to ASR to be lower than 0.10% at 14 days; thus, they used metakaolin mixed fly ash to partially replace OPC and found that the expansion due to ASR was lower than 0.10% at 14 days. The ASR results of mortars containing RA mixed with PA are shown in Fig. 9.

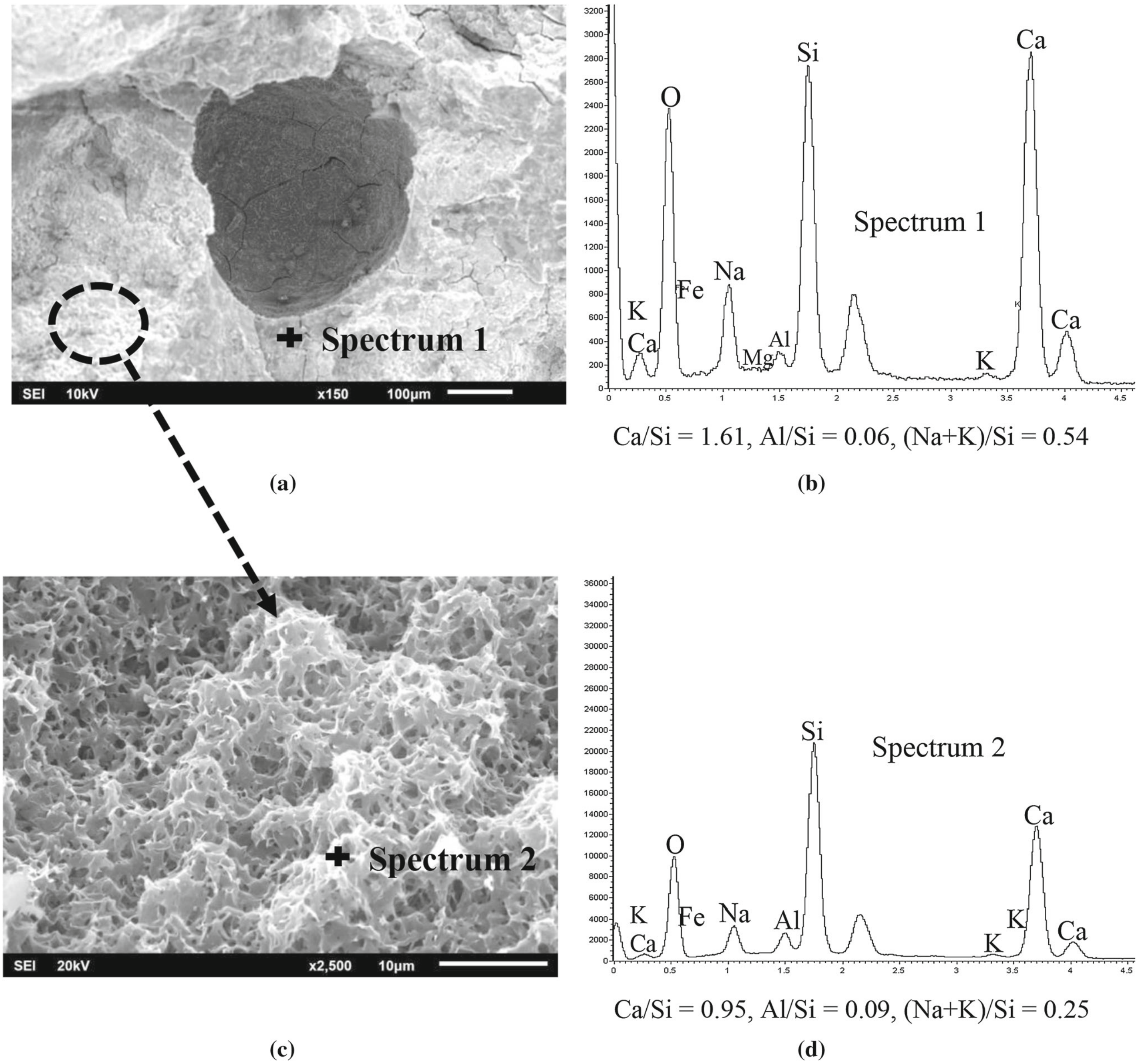


Fig. 12 SEM and EDS of RA20 mortar after 28 days of immersion in 1 N NaOH solution

RA5PA5 mortar (containing RA 5% and PA 5% by weight of binder) had the expansions due to ASR at 14 and 28 days of 0.085 and 0.247%, respectively. The expansion of RA5PA5 mortar was lower than RA10 and CT mortars. Blended cement made from 5% of RA and 5% of PA had little amount of unstable SiO_2 and did not have much affect on the expansion due to ASR. Moreover, SiO_2 in PA could react with $Ca(OH)_2$ to obtain C–S–H. Therefore, the substrates of alkali to react with SiO_2 in aggregate were reduced. The products of C–S–H could make the paste denser, and NaOH solution hardly penetrated to react with the reactive SiO_2. In addition, RA5PA5 mortar had the expansion due to ASR lower than the limit 0.10% (innocuous) as specified by ASTM C1260 [22].

However, the mortars containing RA mixed PA at or above rates of 20% by weight of binder had the expansions due to ASR more than CT mortar. In addition, these mortars had the expansions due to ASR lower than RA mortars but higher than PA mortars at the same replacement rate. The expansion due to ASR of RA mixed with PA mortars increased with the increase in the replacement of RA mixed with PA. Mortars RA5PA5, RA10PA10 and RA15PA15 were not broken due to the reaction between alkali and SiO_2 from RA or from the aggregate, thus, provided lower products of ASR since PA could be used to improve ASR resistance. Although RA

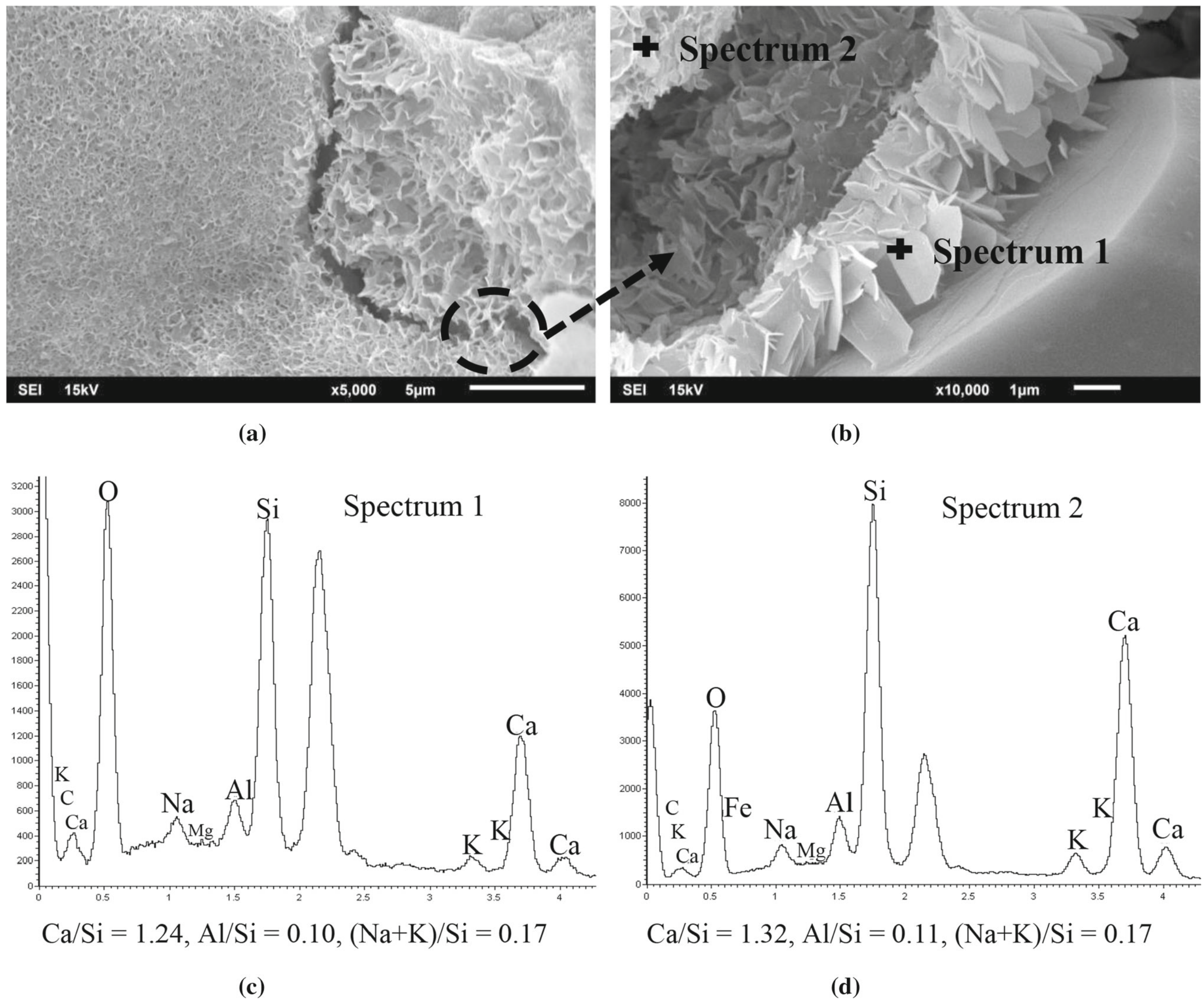


Fig. 13 SEM and EDS of RA mixed with PA (RA20PA20) mortar after 28 days of immersion in 1 N NaOH solution

mixed with PA mortars had lower expansion due to ASR than RA mortars with the same replacement rates of binder, cracks can be easily observed in RA10PA10, RA15PA15, and RA20PA20 mortars as shown in Fig. 10.

3.3 Microstructures of Mortars After Testing for Alkali–Silica Reaction

After testing ASR for 28 days, the highest expansion due to ASR of mortars containing PA, RA, and RA mixed with PA (PA10, RA20, and RA20PA20 mortars) was cut to have dimensions at all sides approximately of 1–2 cm. After that, these part of mortars were prepared for testing of scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometer (EDX or EDS).

The SEM and EDS results of PA10 mortars are shown in Fig. 11. Figure 11a shows microstructure of PA mortar, and ASR products are found, while Fig. 11c is the high magnification picture of ASR products from Fig. 11b. The results from Fig. 11d show the components of Si, Ca, O, and K which confirms the products of ASR. However, the ASR products from fly ash mortar were found to be Si, Na, and Ca elements [36].

For RA mortar, Fig. 12a presents photomicrograph of RA20 mortar which has a void with a diameter of higher than 100 µm and has many microcracks, while EDS in spectrum 1 shows the clear peaks of Ca, Si, and O which are the general products of hydration (see Fig. 12b). Figure 12c shows ASR products in RA20 mortar which is confirmed by spectrum 2 in Fig. 12d, and the ASR products comprise of Si, Ca, and O. Moreover, the chemical composition results from this study were similar to the SEM-EDS results of Zerbino et al. [37] since they also observed the compositions of Si, Na, Ca and Al from EDS results of RA concrete after testing of ASR. In case of self-compacting high-performance concrete made by RA, the elements of Si, Na, Ca and O were found by EDS results [35]. Ca is one important chemical component of ASR gel inside concrete suggested by Knudsen and Thaulow [38] and Fernandes [39] while Lindgård et al. [40] stated that the ASR products in mortar comprised of high amount of Na and low amount of CaO. Moreover, ASR products from many findings had different chemical compositions; thus, it was not a simple method to determine ASR by using the products of chemical compositions.

For RA mixed with PA (RA20PA20) mortar, photomicrographs including EDS of mortar containing RA mixed with PA are shown in Fig. 13a, b and the ASR products are clearly seen in both figures. Figure 13c, d presents the EDS results of ASR products from which the major elements were Si, Ca, and O. It is also noted that the EDS results of ASR product of RA–PA mortar were similar to the EDS results of PA and RA mortars.

The Ca/Si, Al/Si, and (Na+K)/Si ratios are shown in Figs. 10d, 11b, d, and 12c, d. The results showed that the Ca/Si ratio (0.95-1.61) in this study agreed with the results of Duchesene and Bérubé [41] who reported that for ASR of concretes, the Ca/Si ratio of 2.0 for non-blended cement and 1.24–1.46 for blended cement was detected, while the Ca/Si ratio of 1.3 was found by Khan et al. [42]. Moreover, the EDS results in this study were similar to the results obtained by Zerbino et al. [37] and Wang et al. [43]. However, the finding of Fernandes [39] showed that the varying components of ASR product from EDS results were depended on the location of EDS testing; however, they did not show the Ca/Si, Al/Si, and (Na+K)/Si ratios. In addition, Shafaatian et al. [34] showed that the Ca/Si ratios of ASR product were between 0.20 and 0.30, but the Ca/Si ratio did not relate to the expansion of mortar.

The ASR products in this study do not have low Ca of C–S–H for mortar containing palm oil fuel ash (PA) because PA in this study had high Ca (13.3%) and low Si (47.1%); thus, PA produced the C–S–H with high Ca which was conformed to Wang et al. [43] (replace 70% FA) while some of Si in RA could react with NaOH solution (like geopolymer) and then reacted with $Ca(OH)_2$; thus, the EDS results of RA in this study were similar to the results of RA obtained by Zerbino et al. [37].

4 Conclusions

1. The strength activity indices of PA, RA, and RA mixed with PA are more than 75% of the control mortar strength at both 7 and 28 days, indicating that they are good pozzolans for use in concrete (in terms of concrete strength).
2. Ground PA could be used to reduce the expansion of mortar due to ASR (the higher is the replacement of PA, the greater is its effectiveness for controlling the expansion due to ASR).
3. RA mortar had high expansion due to ASR and the use of RA to replace OPC at 20% by weight of binder caused the expansion due to ASR higher than the limitation prescribed by ASTM C1260 [22]; thus, in this study, RA is not a suitable pozzolan to be used in mortar or concrete to reduce ASR.
4. Use of PA mixed with RA to replace OPC could reduce expansion due to ASR of mortar as compared to the use of RA. However, the use of PA mixed with RA at 20% or more to replace OPC in mortar had worse effect due to ASR.

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