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Mechanical performance of modified cement paste made with micro-fine POFA in ammonium nitrate environment

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Abstract

An experimental study was conducted on modified cement paste cubes in ammonium nitrate solution. The modified cement paste was made using micro-fine palm oil fuel ash (POFA) as partial cement replacement. Compressive strength, Energy Dispersive X-Ray (EDX) and a Scanning Electron Microscopy (SEM) test were carried out**.** The 50mm cubes were cast containing 0%, 10%, 20% and 30% of POFA as cement replacement using constant water to cement ratio of 0.4. After 28 days of water curing, 50% of samples were immersed in 20% ammonium nitrate solution and the rest of samples were kept in room temperature. It was observed that, samples replaced with 20% POFA had the highest compressive strength in ammonium nitrate solution. In addition to that, it was also observed through EDX and SEM analysis that cement replaced with 20% POFA had lower Ca/Si ratio and there were more C-S-H structures in the modified cement paste in ammonium nitrate solution. Lower Ca/Si ratio and more C-S-H structures is an indication of higher pozzolanic reactions in the paste.

Keywords: Modified cement paste, Ammonium nitrate, Palm oil fuel ash, Compressive strength, Micro-structure, Pozzolanic

1. Introduction

Agro-industries generally generates large amount of solid wastes which are usually disposed in the environment. These solid wastes are capable of causing severe pollution problem such as land, water, air pollution if it is not managed or treated properly. Palm oil industry is an agro-industry which causes the production of large amount of solid waste. Palm oil fuel ash (POFA) is a solid waste produced from the palm oil industry through the combustion of fibers, shells and bunches (Sata et al., 2007). According to MPOB (2016), there are about 429 palm oil industries in Malaysia which has an annual capacity of 102 million tonnes. POFA produced from the industry is generally black in color. Through lab investigation, black color POFA can be converted into grayish color through heat treatment. POFA is a pozzolanic material, which has a high percentage of alumino-silicate content (Qyeleke et al., 2011). Recently, the use of POFA as a cement replacement has however caught the interest of many researchers because it improves the concrete characteristics. According to Tangchirapat et al. (2007), finer size POFA possess better reaction with cement paste, thus produces concrete having strength higher than coarser size POFA. Kroehong et al. (2011) studied the effect of POFA on cement paste using POFA size of 15.6 and 2.1μm. The authors concluded the paste containing POFA with a greater fineness were denser and more homogeneous which resulted in improved compressive strength of the paste. According to Tangchirapat and Jaturapitakkul, (2010), the degree of fineness of POFA is very significant. When the particles are smaller, they fill the voids in the cement paste, and thus contribute to an increase in the compressive strength. Generally about 20% replacement of OPC with POFA gives better mechanical properties results such as the compressive strength (Sata et al., 2004; Abdullah et al., 2006; Tangchirapat et al., 2009; Kroehong et al., 2011).

Besides reducing the amount of solid waste in the environment, the incorporation of POFA as a cement replacement would also reduce the emission of the green houses gas. When POFA

is used as a cement replacement, the total cement usage is reduced. Hence the production of carbon dioxide during cement manufacturing is also reduced. Carbon dioxide is a major green house gas responsible for the global warming. Therefore, utilization of POFA as a cement replacement would result in a cleaner environment.

Ammonium nitrate is an artificial fertilizer manufactured for the purpose of providing nutrients to plant. According to Milad et al. (2012), ammonium nitrate is highly corrosive material which causes deterioration to concrete structures. The calcium hydroxide in the cement paste is leached out when exposed to ammonium nitrate environment causing, an increase of the permeability and porosity of the paste. According to Arafa et al. (2015), as the concentration of ammonium nitrate increased, the compressive strength decreased. This decrease is due to progressive decalcification reaction which causes more calcium hydroxide to be leached out. When, concrete is exposed to ammonium nitrate environment, the degradation is occurred in two stages. The first stage is known as the decalcification phenomena where the calcium hydroxide is leached out. In the second stage, there is an increase in the volume of the cement paste due to the formation of a new compound and is known as the expansion phenomena Ioan (2013).

Therefore, based on the authors' knowledge, there has been no investigation done using micro-fine POFA as a cement replacement against ammonium nitrate environment. Considering the pozzolanic characteristic of POFA especially when it is fine, it is therefore expected that, the use of micro-fine POFA would give improvement on the mechanical properties of concrete in ammonium nitrate environment. The purpose of this research is to investigate the mechanical and micro structural characteristic of modified cement paste made with micro-fine POFA in ammonium nitrate environment. The use of micro-fine POFA in the cement paste would result in reduction of calcium hydroxide content hence it will be less prone to ammonium nitrate attack.

2. Experimental program

2.1 Materials

2.1.1 Cement

Ordinary Portland cement was used in this research. It was obtained from a local manufacturer, Cahaya Mata Sarawak (CMS) Sdn. Bhd. The cement fulfilled the requirements set under ASTM C-150 Type 1 Ordinary Portland Cement (OPC).

2.1.2 Palm Oil Fuel Ash (POFA)

Palm oil fuel ash (POFA) is a solid waste of the palm oil mill manufacturing process. The POFA used in this study was collected from a local palm oil mill in Kuching, Malaysia. In order to improve its reactivity, the POFA was further treated. The raw, black POFA obtained from the palm oil mill had a median particle size (d_{50}) of 161.92 microns. The POFA was burnt using a furnace at 600^0C for one hour to remove any remaining carbon. The POFA was then ground using a grinder operating at 25,000 rpm for ten minutes to produce POFA particles smaller than 10 microns as known as treated POFA as well as micro-fine POFA.

2.1.3 Ammonium nitrate

Ammonium nitrate was obtained in pellet form the local market. A 20% Ammonium nitrate solution was prepared by mixing the pellets with water. After 28 days of water curing, the 50mm cube samples were immersed in the 20% ammonium nitrate solution for 90 days. The container holding the samples and solution was closed in order to keep the concentration constant. The solution was changed at a regular interval of 30 days to maintain the same effect.

2.2 Mix proportion

Table 1 describes the mix proportion used in this study. Cement was replaced at rate of 0%, 10%, 20%, and 30% of ground POFA having a median particle (d_{50}) size of below 10 micron. A constant water to cement ratio of 0.4 was used for all the mix. Using this mix proportion, 50mm cement cubes were casted. Table 2 shows the curing conditions.

Table 1: Mix amount of modified cement paste for each batch

Mix. No	**Symbol**	**OPC, (gram)**	**POFA (gram)**	**W/C ratio**	**Water (gram)**
1	Control	200	0	0.4	80
2	10%POFA	180	20	0.4	80
3	20%POFA	160	40	0.4	80
4	30%POFA	140	60	0.4	80

Table 2: Curing condition

Moulds	Water	Ammonium Nitrate Solution	Room at ambient Temperature
1 Day	27 days	50% immersed till 90 days	50% left in room till 90 days

3. Test procedures

3.1 Physical properties, chemical compositions and micro-structure properties of POFA

The physical properties consisted of median particles (d_{50}) examined through a particle-size analyser (CILAS 1090 Laser Particle Size Analyser), a specific gravity test in accordance to ASTM D-854 standards and a specific surface area test through the particle size analyser (CILAS 1090 Laser Particle Size Analyser). The chemical composition was determined using X-ray Flourensences (XRF) technique. Consequently, Scanning Electron Microscopy in combination with Energy Dispersive X-ray Spectroscopy (SEM/EDX) was utilized to determine the microscopic image and element composition in POFA and OPC.

3.2 Compressive Strength Test

The compressive strength test of 50mm cubes were carried out. Compressive strength is one of the most important engineering properties used to classify concrete. Compressive strength test was carried out in accordance with BS1881: Part 116: 1983 Standards. Five samples were tested and an average result was calculated. The calibrated compression machine was used for a 50 mm cube test at a loading rate of 700 N/sec., which was within a loading range between 0.2 N/mm^2/sec and 0.4 N/mm^2/sec.

3.2 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray (EDX) Test

A scanning electron microscope (SEM) is a special type of microscope, which produces images of samples by scanning the samples. The electrons connects with the atoms in the sample and produce signals regarding the sample's composition and surface topography. The element analysis and chemical characterization of a sample is determined through EDX technique. The analysis is accomplished by the interaction of some source of x-ray excitation and sample.

In this research, SEM was carried out on modified cement pastes with POFA using a SEM machine. 10mm samples were placed on a double-sided adhesive conductive carbon tape to prevent the scattering of loose particles. The samples were then coated with gold to increase the electrical conductivity in the samples. Several SEM images were made of different aspects of the sample. The SEM machine was set to produce images at 10µm and 1µm.

EDX analysis was carried out in the same machine as the SEM. After producing the SEM images, the samples were further analysed in the EDX test. Each sample was analysed for 10 minutes to determine all elements present in the samples.

4. Results and discussion

4.1 Physical Properties of POFA and OPC

Table 3 presents the physical properties of OPC, raw POFA and treated POFA.

As shown in Table 3, the colour of raw POFA is black due to the presence of excess carbon. This is attributed to the incomplete burning at the palm oil mill. As observed in this study, the colour of treated POFA changed from black to grey after being heated in an electric furnace. According to Table 3, the particle size D_{10}, D_{50} and D_{90} of raw POFA were 96µm, 149µm and 247µm respectively. D_{10} means 10% of the samples tested in the particle size analyzer had a median particle size of 96µm. The mean diameter, which refers to the average value of all particles at 10%, 50% and 90% for raw POFA was 162 µm. For treated POFA, the particles were 0.81µm, 4.92µm and 22.79µm at D_{10}, D_{50} and D_{90}. The mean diameter was 8.7µm.

Table 3 shows the specific gravity of POFA increased as the size decreased. The specific gravity of raw POFA was 1.89 while treated POFA was 2.50. The increase of the specific gravity is due to the grinding process, which produces finer POFA particles. As a result, the

treated POFA are denser and highly packed and have a higher specific gravity value. Similar results have been reported by Sata et al. (2004) and Tangchirapat et al. (2007).

Table 3 also demonstrates the specific surface for raw POFA was 448 cm^2/g while treated POFA had a specific surface area of 53206 cm^2/g. The increase in the specific surface area is due to the reduction of the POFA into finer particles having a higher surface area. For OPC, the particles were of 3.19 µm, 20.22 µm and 52.52 µm at D_{10}, D_{50} and D_{90}. The mean diameter was 24.67µm. The specific gravity and specific surface area were 3.10 and 10667 cm^2/g respectively.

Table 3: Physical properties of POFA and OPC

Physical Properties	OPC	Raw POFA	Treated POFA
Colour	grey	black	grey
Particle Size D_{10} (µm)	3.19	96	0.81
Median Particle D_{50} (µm)	20.22	149	4.92
Particle Size D_{90} (µm)	52.52	247	22.79
Mean Diameter (µm)	24.67	162	8.7
Specific Gravity	3.10	1.89	2.50
Surface Area (cm^2/g) (Particle Size Analyser)	10667	448	53206

4.2 Chemical Composition of POFA and OPC

The chemical composition of OPC and treated POFA is shown in Table 4. Table 4 shows the percentage of SiO_2, the major oxide of POFA, in samples was 58%, and the total sum of SiO_2,

Al_2O_3 and Fe_2O_3 was 62.37%. The loss of ignition of the POFA was 6.78% and SO_3 was 0.7%. The treated POFA however had lower amounts of CaO, 10.8% compared to OPC. In addition, the treated POFA contained 6.1% MgO and 6.45% of K_2O by volume. The POFA in this study is classified as a class N pozzolanic, as the total sum of SiO_2, Al_2O_3 and Fe_2O_3 was close to 70%, SO_3 was lower than 4% and LOI values are close to 10% following ASTM C 618 standards. A similar class was also grouped by Tangchirapat et al. (2009) and Tangchirapat et al. (2012). According to Tangchirapat et al. (2009), the total amount of SiO_2, Al_2O_3 and Fe_2O_3 was 69.7%, while the percentage of LOI and SO_3 was 10% and 0.4% respectively. Tangchirapat et al. (2012) reported the total amount of SiO_2, Al_2O_3 and Fe_2O_3 was 70.3%, while the percentage of LOI and SO_3 was 7.9% and 2.3% respectively.

A low percentage of CaO in POFA signifies the POFA has no cementing properties and therefore the addition of $Ca(OH)_2$ in cement is required for a pozzolanic reaction. A high percentage of silica indicates the pozzolanic characteristic of the POFA. According to Table 4, the percentage of Al_2O_3 and Fe_2O_3 in the POFA was lower than in OPC while, the percentage of K_2O and MgO in the POFA was higher than the OPC. It was reported high K_2O content in POFA is responsible for the increase in the alkali silica reaction damage when reactive aggregate is present Malvar et al. (2006). The SO_3 content in POFA and OPC are almost the same. The LOI in POFA indicates the presence of unburned carbon due to the improper burning process in the palm oil mill. According to Johari et al. (2012), heat treatment influences the LOI values of POFA and is therefore required to ensure compliance with the requirements specified in ASTM C618.

Based on Table 4, it was observed OPC had a high amount of lime (CaO) content, 65.9%. The percent of silica in OPC was relatively low, 19.28% compared to POFA. In addition, according to Table 4, the OPC contained 4.67% Al_2O_3, 3.3% Fe2O3, 1.7% MgO, 0.5% K_2O and 0.3% SO_3 by volume. Generally, OPC should contain the following ranges of

compounds, about 60-67% CaO, 17-25% SiO_2, 3-8% Al_2O_3, 0.5-6% Fe_2O_3, 1-4.0% MgO, 1.3-3.0 SO_3 and 0.4-1.3% alkalis (K_2O & Na_2O) according to ASTM C 150. The chemical composition of OPC in Table 4 however satisfies the required percentage. Similar values were reported by previous researchers (Johari et al, 2012; Usman et al, 2015; Ranjbar et al, 2016).

Table 4: Chemical composition of POFA and OPC

Chemical Composition	**Treated POFA (%)**	**OPC (%)**
Silicon Dioxide, (SiO_2)	58	19.28
Aluminium Oxide, (Al_2O_3)	2.6	4.67
Iron Oxide,(Fe_2O_3)	1.67	3.3
Calcium Oxide, (CaO)	10.8	65.9
Magnesium Oxide, (MgO)	6.1	1.7
Potassium Oxide, (K_2O)	6.45	0.5
Sulphur Trioxide, (SO_3)	0.7	0.3
S+A+F	62.37	N/A
LOI	6.83	N/A

4.3 Scanning Electron Microscopy (SEM) of POFA and OPC

Figure 1 shows the SEM images of raw POFA. The median particle size (d50) of the raw POFA was 161.92µm. Based on Figure 1, the raw POFA had a large particle size and most of the particles were porous. Due to the large particle size, both the specific surface area and specific gravity were lower than the treated POFA. A large porous surface on the POFA particles will result in a greater amount of water used during mixing. Tangchirapat at el. (2007) reported a similar observation for POFA having a median particle size (d_{50}) of 183.0µm.

Figure 2 shows the SEM image of treated POFA. The median particle size (d_{50}) of the treated POFA was below 10µm. It was observed that the treated POFA are smaller in size and shape

compared to raw POFA. The particles were less porous in treated POFA compared to raw POFA. The treated POFA had a wide range of sizes but they were generally irregular and crushed shaped. Both the specific gravity and specific surface area of the treated POFA was higher than the raw POFA. Less water is needed during mixing of the treated POFA due to a less porous texture. It was reported according to literature review that, when the POFA size reduced, the particles became irregular and crushed shape (Tangchirapat et al, 2007; Tangchirapat et al, 2012). The observation of treated POFA in this study agrees with the findings of the previous research.

Figure 3 shows the SEM image of OPC. The median particle size (d_{50}) of the OPC is 24.67µm. The particle morphology of cement consists of a wide range of shapes and sizes but is generally agglomerated shaped. However, it is less porous compared to raw POFA. When water is added, these minerals react and form few hydration products. Ranjbar et al. (2016) reported the particle morphology of cement consists of an agglomerated shape; however, it has a less porous structure compared to POFA. The median particle size (d_{50}) of the OPC used by the authors was 14.6µm.

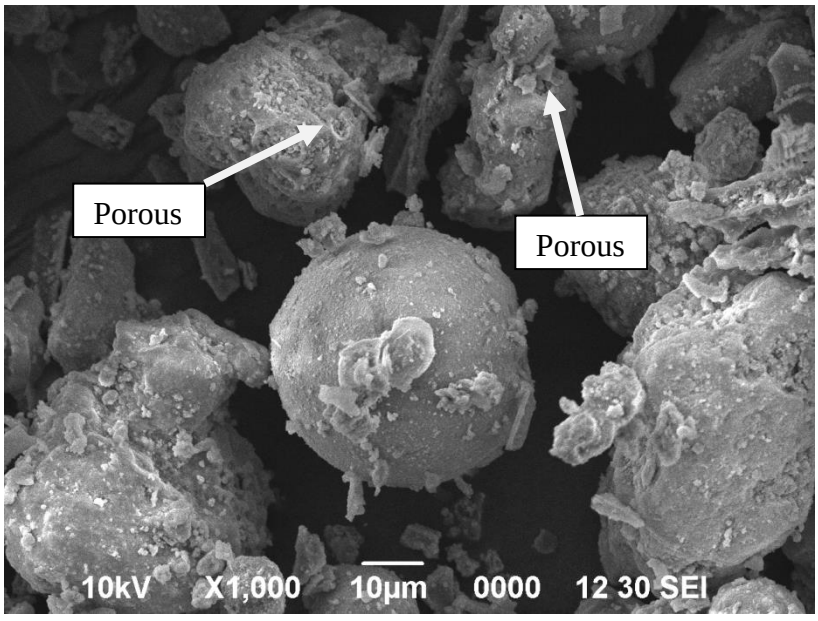

Figure 1: SEM image of Raw POFA

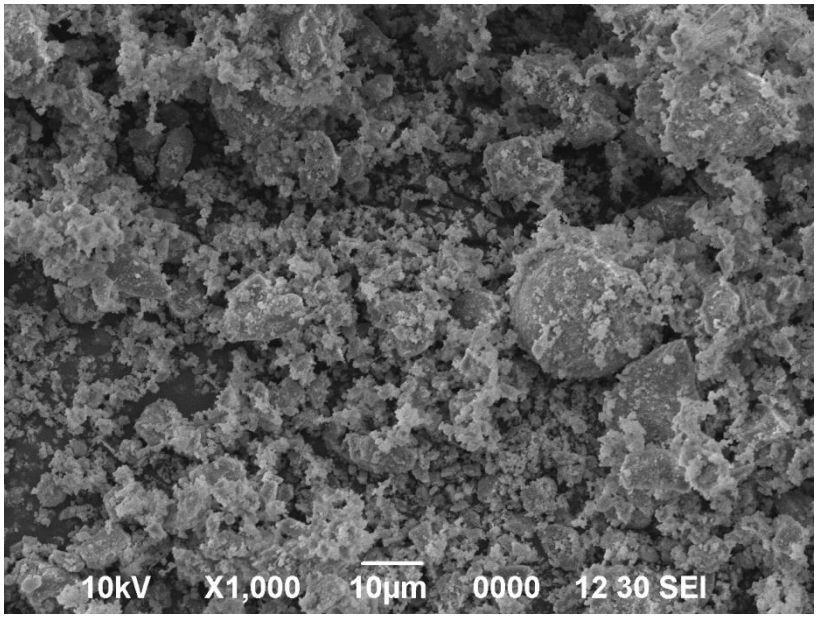

Figure 2 : SEM image of treated POFA

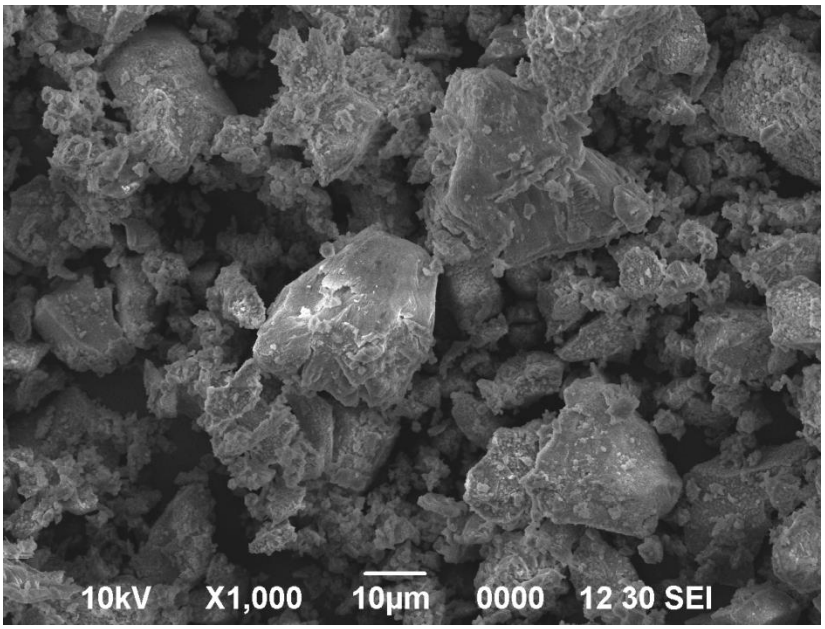

Figure 3 : SEM image of OPC

4.4 EDX Analysis of OPC and POFA

The EDX test results of raw POFA, treated POFA and OPC are shown in Table 5. According to Table 5, the elements found in raw POFA were carbon, oxygen, magnesium, aluminium, silicon, potassium and calcium. It was observed, silicon made up the highest percentage at 30.94% compared to the other elements. The higher percentage of silicon presents the pozzolanic characteristic of POFA. Consequently, the raw POFA particles consisted of 19.97% carbon, 15.93% oxygen, 4.71% magnesium, 2.3% aluminium, 9.88% potassium and 16.26% calcium by volume.

According to Table 5, the percentage of silicon in treated POFA was 36.9%, which was an increase of 19.26% compared to raw POFA. The percentage of oxygen was 25.17% and magnesium 5.24%. Both of these elements showed an increase of 58% and 11.25% respectively compared to raw POFA. As shown in Table 5, the elements carbon, aluminium, potassium and calcium had values of 15.65%, 1.07%, 6.54% and 9.42% respectively in treated POFA. It was observed carbon, aluminium, potassium and calcium decreased by 21.63%, 53.47%, 33.80%, and 42.07% respectively compared to raw POFA. It was observed heat treatment had significantly increased the percentage of silicon and reduced the amount of carbon. These findings agree with previous researchers as shown below.

According to Johari et al. (2012), heat treatment had increased the percentage of silicon dioxide by 27% and reduced the carbon percentage by 99.5%. Johari et al. (2012) carried out an EDX test at three different locations on raw and treated POFA. It was reported that the elements carbon, oxygen, aluminium, magnesium, potassium, silicon, and iron were detected in raw and treated POFA. It was concluded, in raw POFA, the percentage of carbon was higher than in treated POFA. Similarly, the percentage of silicon was lower in raw POFA compared to treated POFA. Usman et al. (2015) also reported finding the elements oxygen,

calcium, potassium, magnesium, oxygen and carbon in treated POFA. They concluded the percentage of silicon was the highest compared to the other elements.

Table 5 illustrates the EDX analysis of OPC. It is noted the elements carbon, oxygen, silicon and calcium were detected in OPC. The percentage of silicon was 5.85%, which was much lower than raw and treated POFA. It was observed calcium had the highest percentage at 56.07% compared to the other elements. Other elements detected were carbon at 7.35% and oxygen at 30.73%. The lower percentage of silicon in OPC is because it does not have any pozzolanic characteristics. The higher percentage of calcium in OPC is required so hydration and a pozzolanic reaction can occur when water and pozzolanic material are added.

Table 5: EDX test result of POFA and OPC

Element	**Atom (%)**		
	Raw POFA	**Treated POFA**	**OPC**
Carbon	19.97	15.65	7.35
Oxygen	15.93	25.17	30.73
Magnesium	4.71	5.24	-
Aluminium	2.3	1.07	-
Silicon	30.94	36.9	5.85
Potassium	9.88	6.54	-
Calcium	16.26	9.42	56.07
Total	100	100	100

4.5 Influence of POFA on the compressive strength of Modified Cement Paste

Figure 4 shows the compressive strength of cement paste at room temperature and in ammonium nitrate solution. Control samples refer to sample kept in room temperature. Based on Figure 4, the compressive strength of the sample containing control- 0% POFA, control-10%POFA, control-20%POFA and control-30%POFA at 3 days is 37.7MPa, 26.2MPa, 20.9 MPa and 20.0MPa respectively. Consequently, the compressive strength at 7 days for control-0% POFA, control-10%POFA, control-20%POFA and control-30% POFA is 47.8MPa, 41.8MPa, 34.4MPa and 24.4MPa. At the 28, 56 and 90 days, the compressive strength had continued to increase for control-0 % POFA, control-10%POFA, control-20%POFA and control-30%POFA. At 28 days, the compressive strength was 50.2MPa, 52.7MPa, 52.0MPa and 41.8MPa for conrol-0%POFA, control-10%POFA, control-20%POFA and control-30%POFA. At 56 days, the compressive strength was 57.5MPa, 57.9 MPa, 60.7MPa and 45.7MPa for conrol-0%POFA, control-10%POFA, control-20%POFA and control-30%POFA respectively. Similarly, at 90 days, the compressive strength was 60.4MPa, 63.7MPa, 69.5MPa and 57MPa for conrol-0%POFA, control-10%POFA, control-20%POFA and control-30%POFA. The compressive strength of the samples however showed a decrease when immersed in ammonium nitrate solution. According to Figure 4, the compressive strength at 56 days for the 0%POFA was 42.7 MPa. Samples replaced with 10% POFA and 20% POFA and 30% POFA had compressive strength values of 47.4MPa, 44.2MPa and 36MPa. At 90 days, the compressive strength of the 0%POFA, 10% POFA, 20% POFA and 30% POFA were 39.2 MPa, 37.4 MPa, 42.4 MPa and 31.8 MPa respectively.

Based on Figure 4, at 56 days, the percentage loss of compressive strength in an ammonium nitrate solution and summarized thus: at 0%POFA, 10% POFA, 20% POFA and 30% POFA the loss of compressive strength was 74%, 82%, 73% and 79%. This comparison was done with the samples in room temperature. Similarly, the loss of compressive strength at 90 days

for 0% POFA, 10% POFA, 20% POFA and 30% POFA were 65%, 59%, 61% and 56% respectively. It was observed the percentage decrease in compressive strength at 56 days in an ammonium nitrate solution was almost 25% compared to samples at room temperature. The strength however continued to decrease to about 50% at 90 days in an ammonium nitrate solution. The compressive strength decreased when samples were immersed in ammonium nitrate solution due to the decalcifications reaction. The lower compressive strength of the samples in ammonium nitrate solution is due to the removal of calcium hydroxide from the paste by the nitrates. Based on these test results it is recommended replacing about 20% of cement with POFA to achieve a better compressive strength value in ammonium nitrate conditions.

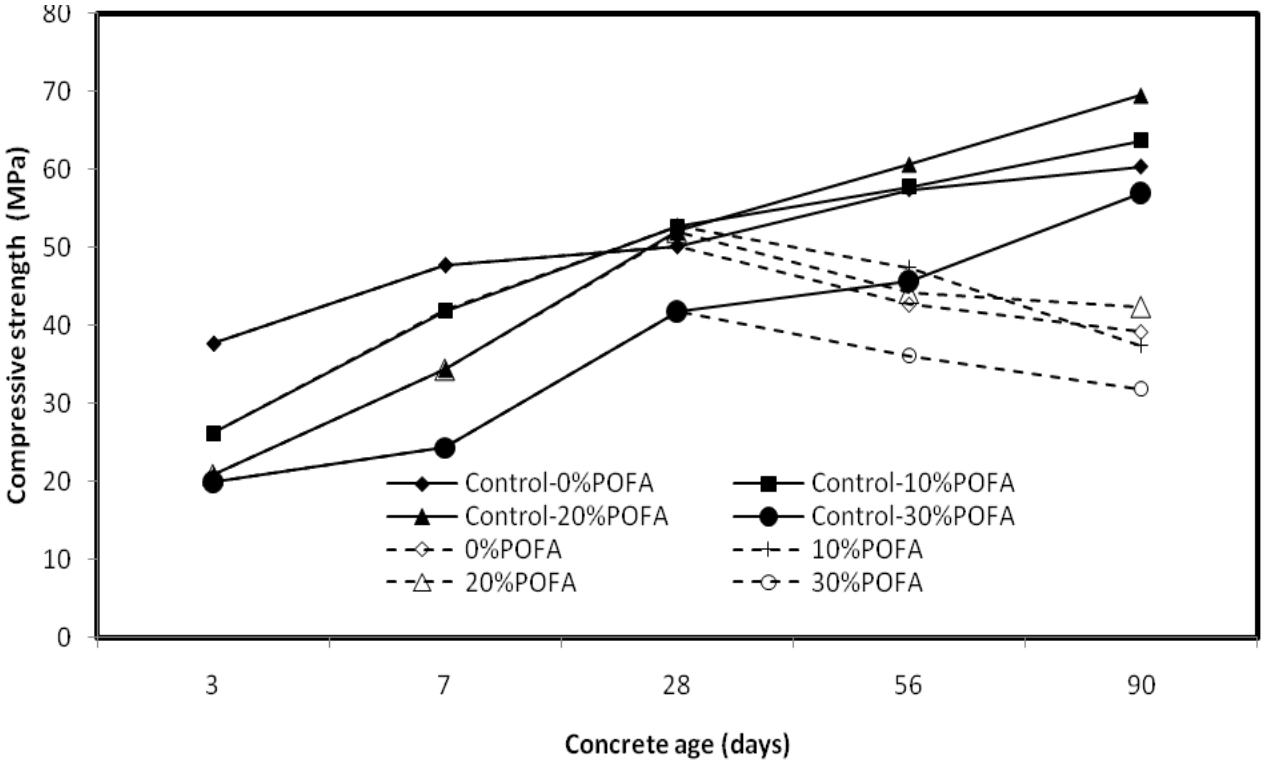

Figure 4: Compressive strength of the modified cement paste

4.6 Energy-dispersive X-ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDX) is a technique used for conducting element analysis. EDX analysis was carried out to identify the total atomic percentage mass of calcium and silicon in the samples at 28 days, 56 days and 90 days, at room temperature and in an ammonium nitrate solution. Based on Table 6, the Ca/Si ratios for the control-0%POFA, control-10% POFA, control-20% POFA and control-30% POFA at 28 days were 3.07, 2.97, 2.17 and 3.91 respectively. At 56 days at room temperature, the Ca/Si ratio of the samples has decreased compared to the 28 days sample due to pozzolanic reactions. The ratio was 2.72, 2.32, 2.71 and 2.90 for the control-0%POFA, control-10% POFA, control-20% POFA and control-30% POFA respectively. Similarly, at 90 days at room temperature, the ratio for the control-0%POFA, control-10% POFA, control-20% POFA and control-30% POFA was 3.79, 2.13, 1.86 and 1.97 respectively. It was observed at 90 days, control-10% POFA, control-20% POFA and control-30% POFA had lower ratio values compared to the 28 days and 56 days samples at room temperature.

The Ca/Si ratio for samples immersed in an ammonium nitrate solution at 56 days was 2.16, 1.17, 1.72 and 2.03 for the 0% POFA, 10% POFA, 20% POFA and 30% POFA respectively. Based on the test results, the Ca/Si ratio for samples at 56 days in an ammonium nitrate solution was lower than the 56 days at room temperature samples. A similar pattern was also observed for the 90 days samples in an ammonium nitrate solution compared to the 90 days samples at room temperature. The Ca/Si ratio was 0.74, 0.69, 0.61 and 0.73 for the 0%POFA, 10% POFA, 20% POFA and 30% POFA for 90 days in an ammonium nitrate solution. The lower Ca/Si ratio for the 56 days and 90 days samples in an ammonium nitrate solution was because of the lower amount of calcium hydroxide present in the paste as the $Ca(OH)_2$ had been consumed by the ammonium nitrate solution. Besides that, the lower Ca/Si ratio is also because of the pozzolanic reaction occurring in the paste. Lower Ca/Si ratio is beneficial as it

is an indication of higher pozzolanic reaction in the paste. In addition, it was also observed with an increase in the curing age, the atomic percentage mass of silicon increases. This is an indication there is more silicon in the paste for the pozzolanic reaction to occur as the curing age increases. Therefore, based on the test results, it is recommended to replace OPC with 20% of POFA for a lower Ca/Si ratio in ammonium nitrate conditions.

Table 6 : Ca/Si ratio of samples with different percentage of POFA at room temperature and in ammonium nitrate solution

Age	Sample	Atomic Mass (%) Silicon	Atomic Mass (%) Calcium	Ca/Si Ratio
28 days	Control-0%POFA	12.84	39.49	3.07
	Control-10% POFA	13.81	41.02	2.97
	Control-20% POFA	16.4	35.61	2.17
	Control-30% POFA	12.45	48.76	3.91
56 days (Room Temperature)	0% POFA	16.09	43.92	2.72
	10% POFA	15.35	35.64	2.32
	20% POFA	15.8	42.94	2.71
	30% POFA	17.61	51.15	2.90
56 days (Ammonium Nitrate)	Control-0%POFA	19.09	41.26	2.16
	Control-10% POFA	26.94	31.68	1.17
	Control-20% POFA	20.06	34.60	1.72
	Control-30% POFA	22.15	45.16	2.03
90 days (Room Temperature)	0% POFA	13.48	51.20	3.79
	10% POFA	15.73	33.52	2.13
	20% POFA	17.23	32.19	1.86
	30% POFA	17.95	35.41	1.97
90 days (Ammonium Nitrate)	Control-0%POFA	30.55	22.74	0.74
	Control-10% POFA	31.19	21.80	0.69
	Control-20% POFA	32.26	19.76	0.61
	Control-30% POFA	34.15	25.00	0.73

4.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) provides sample images which include the chemical composition, orientation and external morphology texture. A SEM test was carried out to detect the $Ca(OH)_2$ and C-S-H in the 0% POFA samples and in samples replaced with 10%, 20% and 30% POFA. Figures 5 show the SEM image of the control-0% POFA at 28 days. For the 28 days control-0% POFA sample, the SEM image in Figure 5 illustrates there is a crystal solid hexagonal plate like morphology. This structure is referred to as $Ca(OH)_2$. In addition, there is also a flowery-like morphology found in the sample. This structure is known as C-S-H. Both $Ca(OH)_2$ and C-S-H are the by-products of cement hydration and are responsible for its strength. It was also observed there are rod-like crystal structures in the 28 days control samples. These rod-like structures are known as ettringite and are usually present in the early stage of the hydration reaction.

According to Figures 6 to 9, it was observed there is an absence of the rod-like structures in the 20% POFA samples in ammonium nitrate solutions. However, it was also observed there is comparatively more hexagonal plate like morphology $Ca(OH)_2$ and flowery-like morphology (C-S-H) in the 20% POFA samples compared to the control-0%POFA sample. This is evidence of the pozzolanic reaction. Moreover, it was observed there was a higher amount of flower-like morphology in the 90 days 20% POFA sample compared to 56 days 20% POFA samples. This can attribute to a higher pozzolanic reaction as the curing age increases. The findings in this study agree with the previous research studies. According to Hussin et al. (2015), when increasing the age of curing, the total amount of calcium silicate hydrate crystal increased.

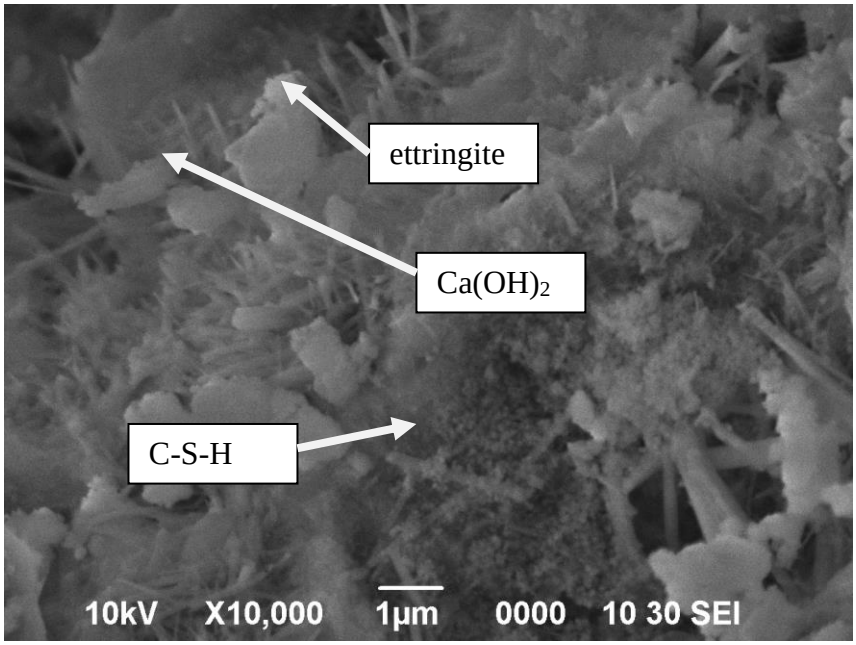

Figure 5: SEM of control-0%POFA at 28 days

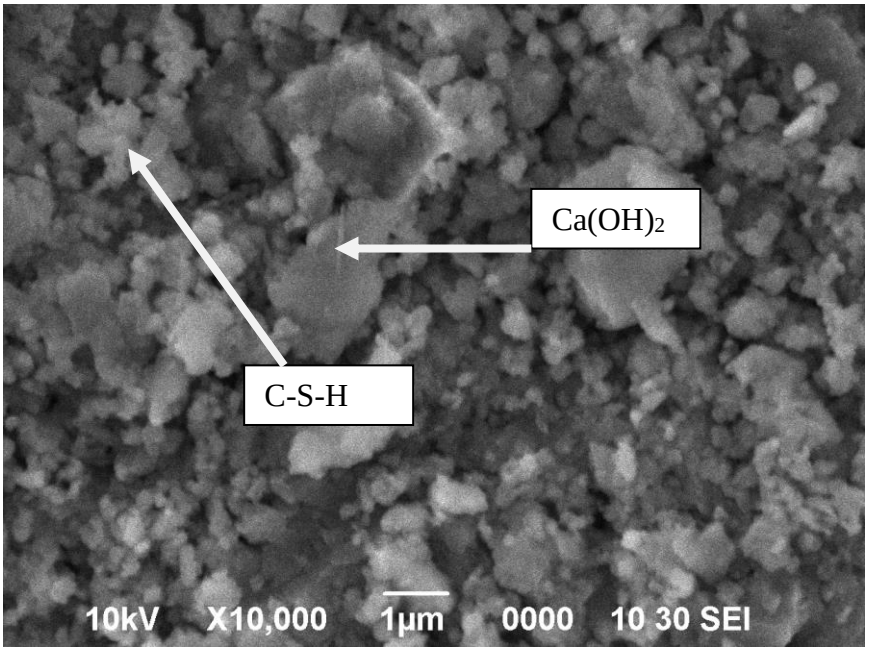

Figure 6: Control-20% POFA at 56 days

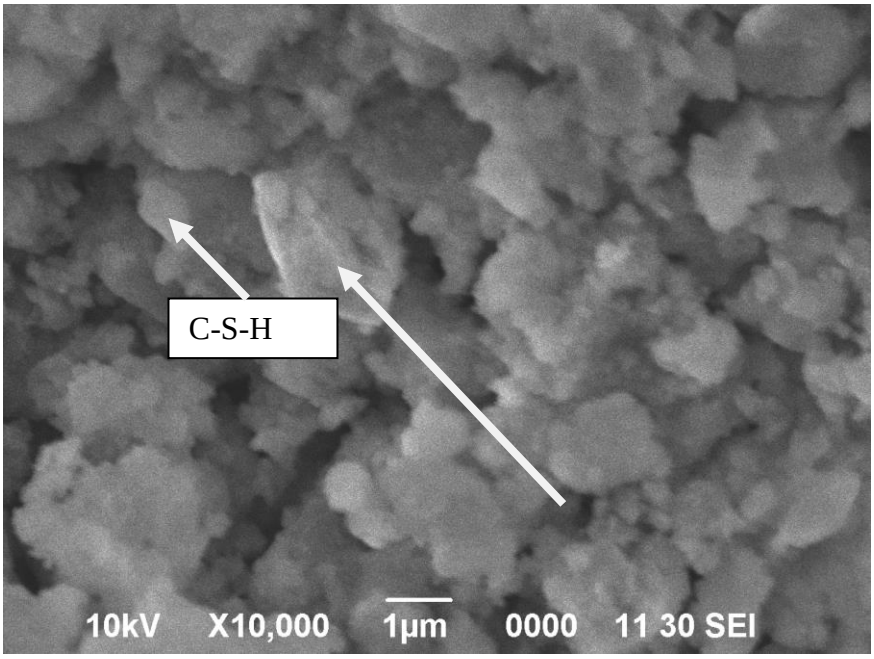

Figure 7: 20% POFA at 56 days (ammonium nitrate solution)

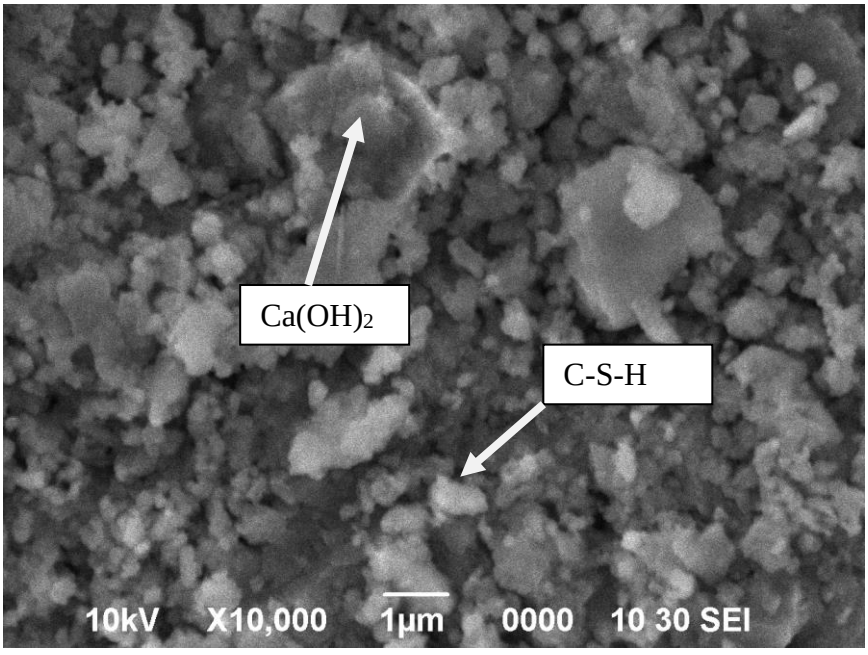

Figure 8: Control-20%POFA at 90 days

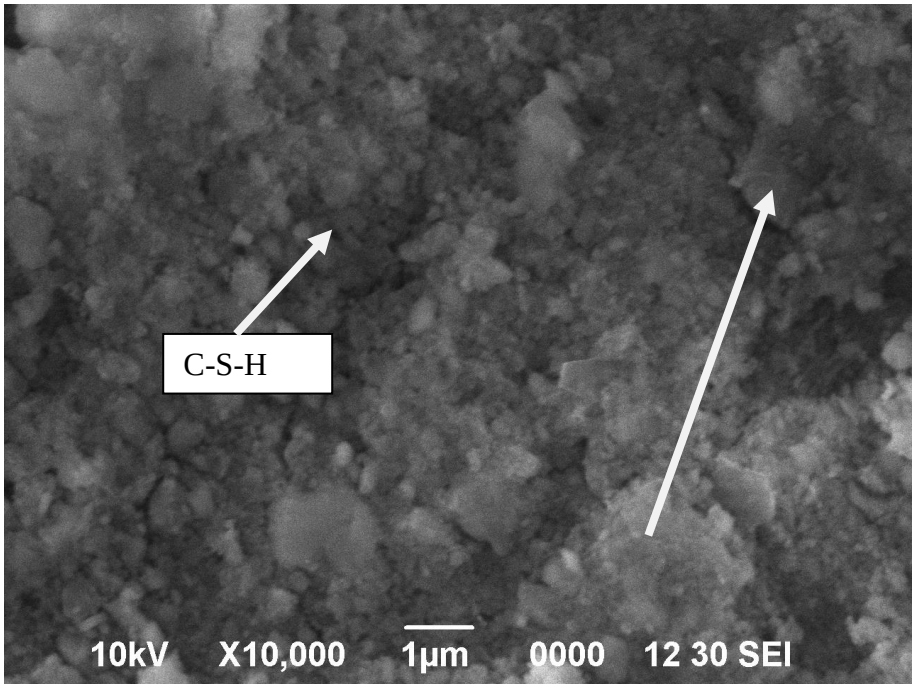

Figure 9: 20%POFA at 90 days (ammonium nitrate solution)

5.0 Conclusion

Based on the laboratory investigation, the following conclusions are drawn:

- Grinding significantly improves the specific gravity and specific surface area of POFA. The specific gravity and specific surface area are highly influenced by the size of the POFA. The finer the POFA, the higher the specific gravity and specific surface area, when compared to coarser POFA. Finer POFA particles have fewer voids, which cause the POFA particles to be denser and more packed compared to coarser POFA.

- Heat treatment at 600 degrees Celsius for one hour increased the main oxides of POFA, particularly silica and reduced the carbon content. Based on its chemical composition, the treated POFA is classified as an N class pozzolan.

- The compressive strength decreased when samples were immersed in an ammonium nitrate solution due to the decalcification reaction. The calcium hydroxide in the cement paste had been consumed by the nitrate in the ammonium nitrate solution, therefore the compressive strength decreased. Cement paste containing 20% POFA in an ammonium nitrate solution exhibited highest compressive strength of 42.4MPa at 90 days.

- Based on Energy-dispersive X-ray spectroscopy (EDX) test results, it was observed that, the Ca/Si ratio decreased when the volume of calcium silicate hydrate increased. Consequently, the Ca/Si ratio increased when the volume of calcium hydroxide increased. Calcium silicate hydrate (C-S-H) is classified by the Ca/Si ratio. Cement replaced with 20% POFA exhibited a lower Ca/Si ratio due to a higher pozzolanic reaction in ammonium nitrate solution

- The SEM test results also demonstrated a 20% POFA -based cement paste produced more C-S-H compared to the control sample causing the matrix to be denser and hence it provided better resistance in ammonium nitrate solution.

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